PETROLEUM AND NATURAL-GAS RESEARCH PROGRAM, BUREAU OF MINES FISCAL YEAR 1953

BY R. A. CATTELL AND OTHERS

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by

R. A. Cattell[1] and others

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SUMMARY AND INTRODUCTION

Continuing progress in a petroleum and natural gas research program of world-wide significance makes it difficult to pinpoint accomplishments within definite time limits, and it is helpful to look back as well as forward in attempting to introduce and summarize the petroleum work of the Bureau of Mines in the fiscal year 1953. The 1952 report2/ indicated progress in a long-range program applicable in large part to both defense and peacetime requirements. The present report indicates a continuation of that program, modified partly by new demands and interests of government and industry, and is highlighted by a number of significant contributions to the knowledge of petroleum and natural gas and their production and utilization.

The intent of the program was clearly epitomized in a statement made near the end of the fiscal year at a general conference of Bureau of Mines personnel where the record was critically reviewed:

> In order that collectively and individually the Bureau staff concerned with petroleum and natural gas research will better fulfill the requirements of the existence of this agency, broaden the horizons of thinking with regard to cooperative research with industry and others, and arrive at a consolidated and coordinated program to meet the needs of the United States and the other free nations for petroleum and natural gas and their products.

For those who feel that we may have found the last of our deposits, it may be heartening to take note of the observation of W. W. Keeler, vice president, Phillips Petroleum Co., who said recently:

> I believe that the petroleum industry is still largely in its infancy, and that its greatest era still lies before it. Nearly all of the present wide range of operations and products of the industry have been developed within the lifetime (of this generation). In fact, the majority of these developments have occurred since the time we began our careers. A vast multitude of processes and products are now in the idea, research, or pilot plant stage. It seems that nearly every pursuit of some research project turns up a number of other possibilities which themselves merit new research projects.
>
> There appear to be no ultimate limits to the ways in which hundreds of hydrocarbons in petroleum can be rearranged, combined, reacted, and processed into useful products. Our challenge lies in the training and ingenuity it will take to continue the accelerated pace of these developments.
>
> Likewise, there is no apparent limit to the oil and gas resources which form the basis for these developments, despite the fact that nearly ever since the first crude oil was discovered in 1859, so-called experts have been predicting that we are running out of oil.***

2/ Cattell, R. A., and others, Petroleum and Natural-Gas Research Program, Bureau of Mines, 1952, Bureau of Mines Inf. Circ. 7659, 1953, 46 pp.

Thus, it would seem that a broad field lies ahead to be explored in many particulars. An annual report of a research organization's activities, without too much emphasis on definite end points, is an excellent time to take stock in order to orient the planning. It gives an opportunity for this Federal agency to determine the best course for it to follow across the broad field so well pictured in bold strokes by Keeler.

The petroleum engineering study of the Big Lake field, Reagan County, Tex., suspended for 2 years in order to fulfull more immediate assignments, has been completed, and the report is in final stages of preparation. The study gives the history of the first of 55 Ellenburger reservoirs in West Texas to reach near depletion and will help operators to gain maximum recoveries from the remaining Ellenburger fields or from future discoveries in that productive horizon.

In cooperation with the Arkansas Oil and Gas Commission, an engineering study of the Buckrange sandstone reservoir in the Stephens field, Columbia, Nevada, and Ouchita Counties, Ark., has been initiated. With production by primary methods near the economic limit, the Bureau will study the field history and characteristics and the feasibilities of secondary recovery methods to produce part of the estimated 100 million barrels of oil still in the sandstone.

Although field work was completed on the Scurry Reef reservoir in Scurry and adjacent counties in Texas during the preceding year and several reports thereon were submitted to the Petroleum Administration for Defense - whose needs for information on the area initially prompted this work by the Bureau of Mines in cooperation with the United States Geological Survey - the data collected by the Bureau continued to be of outstanding assistance to the Scurry Area Canyon Reef Operators Committee (SACROC). The data were used extensively in the efforts of SACROC to unitize the area and initiate a pressure-maintenance program, which it has estimated will increase the ultimate recovery from the SACROC unit alone by at least 720,000,000 barrels of oil. The Bureau has cooperated in every possible way to make its engineering findings available to all persons concerned with developing this large reserve. Also, the Texas Railroad Commission had access to the Bureau of Mines data to assist in its rulings on the operation of this vast oil reservoir.

A report published during 1953 on the water characteristics of several producing formations in Scurry and adjacent counties should be valuable in solving production problems, particularly those involving pressure-maintenance projects where water is to be the injection medium. Oil and gas separator temperatures and pressures in the Scurry Reef field and their effect upon gas-oil ratios, specific gravities of separator gas, formation-volume factors, and API gravities of stock-tank oil were studied. The results should point the way to greater conservation in this and other fields.

A report is in preparation showing the long-term effect of a pressure-maintenance program on oil production from the Basal Sundance sand in the Lance Creek field, Wyo. Laboratory experiments and laboratory analyses of samples taken in 1937, 1941, 1947, and 1948 from wells in the field show that reservoir behavior under the influence of gas injection for pressure maintenance can be predicted from the laboratory studies, and a forecast can be made of the additional oil available by pressure-maintenance operation. Additional studies in the laboratory are in progress on the rate of vaporization that occurs as gas is cycled through a laboratory reservoir during a simulated pressure-maintenance program. The results should stimulate interest in gas-injection projects as one means of increasing ultimate oil production.

The results of research on specific volumes and phase states of natural gas and gas-condensate fluids have been correlated to provide diagrams that will indicate the properties of these fluids at reservoir conditions when only the composition is known. A monograph, Phase Relations of Gas-Condensate Fluids, well toward completion, will show correlations for two-component and multi-component systems encountered in natural gas and condensate production and will show by detailed examples how these correlations are to be applied to practical problems. With some 610 figures and tables, the monograph will be a guide to the operation of gas-condensate fields for maximum yields with maximum economy.

A study of the flow of natural gas in the producing strings of gas wells was completed and friction factors now can be calculated for all sizes of gas-well tubing and casing. These friction factors can be used to measure the productivity of natural gas wells, as well as for other gas-flow problems. A report also was completed on a study of the magnitude of the amount of supersaturation that occurs in an underground reservoir during the flow of oil and gas to wells and of the amount of undersaturation that exists during repressuring of an oil reservoir.

The Spraberry area of West Texas has been characterized as having one of the largest deposits of petroleum in this country, but it is unobtainable by present production methods. The nature of the formations and the difficulty of extracting the oil that is known to be contained in the reservoir rocks in the Spraberry area fields have called for ingenuity and new concepts of oil production by the industry. Because of the experience obtained in the Scurry Reef area, Bureau engineers felt that their methods of pressure-buildup testing to determine the effect of well-completion methods on well productivity, resulting from cooperative work with the American Gas Association, might have application in the Spraberry area. Accordingly, a series of tests was begun, but before the tests were completed on 14 wells to determine their well-completion efficiencies, the Texas Railroad Commission issued an order, effective April 1, 1953, shutting in all Spraberry wells, which was evoked to prevent physical waste until the companies provided facilities to handle the gas being vented to the air. However, the Commission granted two exceptions to permit the Bureau to complete its field testing. This evidence of the Commission's recognition of the value of the Bureau's work in this area is particularly noteworthy in view of the engineering, legal, and economic factors involved.

Other cooperative research with the American Gas Association continued. Of special interest to gas-pipeline operators was the completion of the field tests on the flow capacity of seven experimental pipelines at Goleta, Calif., which were made to develop more reliable standards for estimating the flow capacities of planned pipelines and the efficiencies of existing pipelines. To obtain basic data for comparative purposes on the gas transmission characteristics of commercial pipelines, tests also were made on 120 feet of super-smooth pipe honed to a "mirror" finish at the Naval Gun Factory. At the conclusion of the work, the equipment was dismantled.

Studies of well-completion methods in California showed that it is possible to calculate the permeability of a producing formation to oil from the rate of pressure rise in a well after production is halted. Tests also confirmed the detrimental effects from the invasion of filtrates from water-base drilling fluids into certain producing formations. Proper completion methods assure longer flowing life and increased total recovery.

An extensive study of multiphase flow and the problem of spacing oil wells was completed and will be published as a Bureau of Mines bulletin, combining and coordinating the scientific and practical aspects of the problem in one report. Work was continued on correlating the water contents of oil-base core samples, as determined by distillation with water saturations determined by: (1) Capillary displacement of interstitial water by air; (2) displacement of air from a clean extracted core by mercury; (3) evaporation of liquid from the pore space of a core sample; and (4) centrifuging liquid from the pore space of a core sample.

Investigations of substitutes for quebracho as a component of drilling fluids were published, indicating that 75 materials tested included 15 that could be considered as substitutes, although none equaled quebracho in effectiveness. Relative merits of the 15 materials are tabulated.

Recognition of the importance of the effect of naturally occurring clays on the flow of oil through reservoir sands and on the displacement of oil by water in secondary recovery has resulted in the expansion of clay studies by the Bureau of Mines. The Bureau helped sponsor the First National Conference on Clays and Clay Technology in Berkeley, Calif., during the year, and one day of the meeting was devoted to the function of clay minerals in the petroleum industry.

Fluid injection may be more in line with an exact technical description of the processes now used to increase production in partly depleted fields, but "secondary recovery" is a term that is so implanted in the conversations of field men and in technical writings that it would be difficult to divorce the term from association with activities of the Bureau in the so-called stripper fields. At one time, projects designed to obtain higher ultimate recovery of oil by injecting gas and air, and more recently by injecting water, were primarily the concern of small operators who lacked adequate engineering and research personnel and facilities. This situation is changing rapidly as it is becoming more generally recognized that fluid-injection methods, which were developed in stripper fields, often are applicable, with some modifications, to flush fields and that it is more economical and practical to apply stimulative methods early in the life of the field so as to recover all available oil in one operation. For these and other reasons, the techniques as applied to secondary-recovery operations in the shallow stripper fields and fluid-injection projects in flush fields are growing more and more alike. Many of the larger oil companies now have developed research organizations to study old and to devise new stimulative methods. Both the large producers and the small operators for many years have watched the oil-production decline curves smooth out and finally, because of increased energy applied through fluid injection, have watched the production curve rise again to new highs.

The study of the Healdton oil field in southern Oklahoma, mentioned as being underway in last year's report, attracted widespread attention when the Bureau's work was completed and publicized. This field has been of interest to Bureau engineers for many years, and various studies were initiated at different times, but the results were not published because the findings were inconclusive. However, after a long and painstaking search for all known data, the report now available brings into the limelight an area where a large quantity of oil will be recovered by applying stimulative methods under good engineering supervision. Several oral summaries of the report have been given before technical and operating groups, and the Bureau has been commended highly because of the completed study - an assignment that no other group was in a position to do.

Because of the success of Bureau engineers in handling the large area of the Healdton field, and in response to the requests of numerous oil producers, a petroleum-engineering study of another large area in Oklahoma, namely, the Cushing oil field in Creek County, which has added so much to the Nation's wealth in oil and to the colorful petroleum history of the country, has been begun. This is the largest engineering-field study of a field nearing depletion by primary methods so far undertaken by Bureau engineers, and the results of the work should play an important part in increasing the recovery of large petroleum reserves that still remain in the reservoir, although nearly 400 million barrels of oil have been recovered by primary-production methods. The field covers nearly 25,000 oil-productive acres on which about 4,000 wells have been drilled. The area has long intrigued Bureau engineers, but because of its diversified ownership and the complexities involved in obtaining the essential engineering data, the field study was postponed until near the end of the fiscal year 1953.

Petroleum-engineering studies of the Flat Rock and Quapaw fields in Osage County, Okla., indicate that additional oil can be recovered by water flooding but that not all of both fields would be suitable for water flooding and that the additional oil recovered would not approach percentage-wise recoveries in other types of fields that have been successfully water flooded.

The report on the KMA field in northern Texas is another example of benefits derived from an engineering study of a large oil-productive area by an impartial and disinterested team of Bureau engineers. It has been well established that information in the report was instrumental in initiating several successful water floods in parts of the KMA field. These projects might have been delayed unduly if the possibilities of greater oil extraction had not been brought to the attention of the industry in this report, which was made possible through the cooperation of the North Texas Oil and Gas Association. Data are being gathered on 60 floods in 22 counties of North and West Central Texas with the view of preparing technical reports that will point out successful floods, give the reasons for the failure of some water floods, and present generalized summaries of water-flooding activities in the area.

A personal touch is given to some of the work of the Bureau pertaining to secondary-recovery projects by the annual tours conducted in northeastern Oklahoma and eastern Kansas. For the fourth consecutive year, Bureau of Mines engineers arranged a tour of outstanding water-flooding projects. This year the tour was in northeastern Kansas and was attended by 225 oil men, and the convoy included 75 automobiles. Not only was there a published report available for distribution to describe the properties, but engineers of the respective operators, the authors of the Bureau report, and others familiar with the projects engaged in discussion using a portable public address system, making it possible for everyone attending to get first-hand information on equipment, methods, and results.

Because water has become so important a factor in secondary-recovery operations, interest has grown amazingly in treating water to improve its efficiency in forcing more oil from the producing formations. A report on this subject caused widespread interest, and summaries of it were presented orally to large groups throughout the Midcontinent area. This method of spreading the gospel of conservation by word of mouth to augment the printed word is becoming increasingly important, and more attention is being given to the oral dissemination of information.

Tracing the flow of water through oil sands using radioactive isotopes, and the detergency of certain additives to water in flooding operations are two other lines of research of the Bureau. These distinctive research projects are conducted at Bartlesville, Okla., and the research workers have received many inquiries concerning the progress of the work.

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Accurate evaluations of water saturations in the partly depleted oil reservoirs of the eastern United States are most important in selecting projects in which water flooding will successfully yield more oil. Currently a shielded monoelectrode system is being used to obtain logs from which water saturations can be determined. The system was field tested on eight wells in the region with good results.

The results of laboratory and field experiments at Franklin, Pa., conducted to study the effects of plugging oil reservoir sandstones with metallic oxide smoke to prevent bypassing during gas injection were published. These results indicate that titanium dioxide used in conjunction with ammonium chloride will plug gas-injection wells selectively but that pure materials and great care are required. Basic studies relating to shooting oil and gas wells with explosives were continued. Techniques and apparatus for strain and pressure measurements in deep, liquid-filled holes were developed and used in field experiments, and studies were continued on the effect of oil and water saturations on rock properties.

In California experiments were conducted to evaluate the fundamental properties of reservoir rocks in that region that influence oil recovery by water flooding. The work included measurement of surface areas of sands and clays in the laboratory by an improved technique and a study of the pore geometry of cores from California formations. The study of the effect of oil viscosity on oil recovery disclosed that the surface tension between oil field brines and oil has a much greater influence on oil recovery than has been realized. The continuing study of oil recovery by gravity drainage indicates that for some lighter oils and certain formations gravity drainage will allow larger ultimate recoveries than water flooding. Gravity drainage decreases as the viscosity of the oil increases and the quantity of interstitial water increases. Large sand grains allow greater recovery, as does increased formation thickness.

During the year, 209 domestic crude oil samples and 4 foreign ones were analyzed by the Bureau of Mines routine method, and reports of many analyses were published or were in preparation for publication. The regular periodic surveys of characteristics of motor, aviation, and diesel fuels were published, with octane numbers for motor fuels continuing to reach new highs.

The study of sulfur in petroleum, conducted with the American Petroleum Institute, continued to show significant progress. Five additional pure sulfur compounds were made available for distribution to laboratories throughout the world as standards for instrument and analytical method calibration. Physical property and spectral data for these and other sulfur compounds also were published. Further work on the occurrence of elemental sulfur showed that some crude oils contain 1 percent or more of elemental sulfur. Careful analytical study of a Wasson, Tex., crude oil resulted in the identification of virtually all the theoretically possible sulfur compounds boiling below 100° C. in the oil. Some of these compounds never before had been identified in any crude oil.

The acquisition of fundamental information pertaining to sulfur in petroleum languished for many years. However, with tools now at hand it is possible to make progress in research unheard of in the 1930's by the then laborious methods, which limited the scientist's ability to look deep into the heart of the problem. In the 5 years since API Project 48 was begun, more progress has been made in ascertaining the real truths regarding sulfur-in-petroleum than had been obtained from the time that the sulfur problem first was recognized in the Lima, Ohio, field about 1885 and the beginning of this research project in 1948.

In a study of nitrogen constituents of petroleum, a systematic method for types of nitrogen compounds was devised and applied to the analysis of 34 diesel fuels undergoing stability in storage tests.

The work on the composition, stability, and combustion of diesel fuels continued at a high level, sponsored by industrial organizations such as the Western Petroleum Refiners Association and the Coordinating Research Council and, Government agencies, represented by the Bureau of Ships of the Navy. Evidence of the interest of both automobile manufacturers and petroleum refiners was given at the Seventh Annual Diesel Conference attended by 122 leaders of these two industries. A panel discussion of the physical and chemical processes that occur during the preflame and inflammation periods in diesel-engine operation was conducted on the first day, and the second day was given over to the presentation of the findings of the Bureau of Mines during the last year relating to the stability and incompatibility of diesel fuels. The chief of the engineering department of one of the large motor companies of the country in reviewing the situation stated in part: "My own reaction, as well as that of other people who have talked to me, shows that the conference fills a definite void in our professional meetings."

The thermodynamics laboratory through the years has evolved a complete and integrated program of thermodynamic studies pertaining to petroleum and sulfur compounds. In papers now being published on the thermodynamic properties of sulfur compounds are found all of the experimental data and theoretical interpretations that are required to obtain values of the thermodynamic properties over the whole useful temperature range. In contrast, a person wishing to consult the original literature on one of many of the common hydrocarbons would have to consult half a dozen or more different publications prepared by as many different laboratories to obtain all of the same kinds of data for the compound under consideration.

During the year low-temperature calorimetric studies were completed for 10 compounds, heats of combustion were determined for 5 compounds, 4 of which were sulfur compounds, the vapor heat capacities of 6 compounds were obtained, and statistical mechanics were utilized to give thermodynamic property tables to 1,500° K. for 8 hydrocarbons and sulfur compounds.

By way of reciprocal exchange in connection with the International Union of Thermochemistry and visits by 3 professors from the University of Lund, Sweden, with whom the Bureau thermochemists have collaborated, the chief of the Thermodynamics Branch spent 6 weeks in Europe attending meetings of the International Union of Pure and Applied Chemistry held in Stockholm and representing the Bureau of Mines at the biennial meeting of the International Commission of Thermochemistry. In addition to visiting laboratories in England, France, and Holland, he visited the University of Lund to obtain first-hand information on recent work that the Swedish investigators are doing in combustion calorimetry with a rotating bomb. The University of Lund and the thermodynamics laboratory of the Bureau of Mines at Bartlesville, Okla., are the only places in the world where a special study has been made of the heats of combustion of sulfur compounds. The close relationship that has been established between the two laboratories has been instrumental in perfecting a very difficult technique that is already producing a steady flow of data useful to science and to industry.

Another evidence of international cooperation in scientific fields was the assignment of French engineers to the Petroleum Experiment Station in Bartlesville, Okla., for a training period. Two of these young engineers, one from the French Petroleum Institute and another from a French-operated company in Morocco, were members of a French mission comprised of eight engineers in this country under the

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sponsorship of the Mutual Security Agency. The two engineers assigned to the Bureau spent their training period at the Petroleum Experiment Station acquiring information on research in reservoir performance and on petroleum production methods and in visiting oil companies in the Midcontinent area. Still another evidence of good will was a visit from another foreign mission comprised of industrial engineers from France, Italy, and Germany who were concerned with corrosion problems. Dr. Ferdinand Freidensburg, Mayor of West Berlin during the airlift operation and a professor of mineral economy at the University of Berlin, visited the Bartlesville Station as a part of his tour of various headquarters of the Bureau of Mines under the sponsorship of the Department of State. In addition, during the International Petroleum Exposition, there were many casual visitors from foreign countries who spent from one to several days at the station as a part of their education in American ways of dealing with petroleum.

The International Petroleum Exposition in Tulsa afforded the Bureau an opportunity to display some of its activities through visual education. With representation on the IPE technical committees for both production and chemistry and refining, the Bureau contributed 4 outstanding items in the Hall of Science, which was primarily an educational display of advancements in petroleum science and technology during the last 5 years. The first exhibit was that of the shot-hole caliper. A transparent lucite window allowed the observer to see the caliper raised and lowered in the 2-inch "hole" and to view the expansion and contraction of the 4 measuring arms, which extend to a maximum radius of 36 inches.

A diorama of an oil field with cutaway section into the oil-producing strata showed in miniature the operation of tracing water movement with a suitable radioisotope. The various steps in the operation were described by a sound-recording mechanism.

The third exhibit included a windowed vessel and other equipment for demonstrating the phenomena of the dew point, bubble point, and critical state of hydrocarbon fluids such as may occur in natural petroleum reservoirs. A mirror was provided through which visitors could view the color and phase changes without being in any danger from the pressure within the vessel.

The fourth exhibit was a finely coordinated and colorful display of crude oils from all over the world and a display and demonstration of the highly scientific instruments now required to analyze petroleum.

With reference to better tools and the increasing cost of research, it has been noted in recent conference discussions that great advances have been made in ascertaining some of the types of hydrocarbons that are present in fractions from a single crude oil. Research tools are now available whereby excellent results might be expected from a coordinated study of the composition of the higher boiling fractions of crude oil. This research is probably more than any one company would wish to carry out by itself, yet it is a problem that all companies would like to see studied because the information is vital to the manufacture and uses of lubricating oils - a subject in which Bureau chemists are intensely interested and a research project that might well be conducted by the Bureau of Mines.

Repeating an earlier suggested thought that it is not always possible to dateline accomplishments, the apparent ones of the past 12 months are set forth in the following sections: Oil and Gas Development and Production, Secondary Recovery, Petroleum Chemistry and Refining, Thermodynamics of Petroleum, and Transportation of Natural Gas.

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This annual report of the Bureau's petroleum-research and natural-gas-research activities was prepared from reports submitted by the scientific staffs in 5 field headquarters in 4 of the Bureau's 9 regions and by the staff of the Director's office in Washington. Acknowledgment is made to the following regional directors and their staffs for their valuable assistance:

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OIL AND GAS DEVELOPMENT AND PRODUCTION

Petroleum-Engineering Studies

Big Lake Field, Tex.

The petroleum-engineering study of the Ellenburger reservoir in the Big Lake field, Reagan County, Tex., was reactivated after being suspended for about 2 years because of the necessary assignment of the personnel to study the Scurry Reef Reservoir.

The manuscript, now in the final stages of preparation, sets forth the characteristics of the Ellenburger reservoir in this field, describes the production history, which started in 1928, and presents calculations used in estimating the recovery that has been obtained and the probable recovery that could have been realized if the field had been operated with production techniques now used, which were unknown when this reservoir was discovered. This is the first of approximately 55 Ellenburger reservoirs in West Texas to reach near depletion. Over 30 million barrels of oil have been produced from the reservoir, and it is believed that the experience regarding recovery and operation practices in the Big Lake field should prove helpful in many respects throughout the West Texas area where most of the present oil reserves are found in fractured limestone, which cannot be evaluated by core analysis.

Stephens Field, Ark.
(Buckrange Sandstone Reservoir)

An engineering study of the Buckrange sandstone reservoir in the Stephens field, Columbia, Nevada, and Ouachita Counties, Ark., is in progress under a cooperative agreement with the Arkansas Oil and Gas Commission. The study was undertaken to determine the feasibility of secondary recovery of part of the large amount of oil reportedly left in the reservoir. Production by primary methods is near the economic limit. An engineering report will be published giving statistical and other data describing reservoir conditions and suggesting secondary-recovery possibilities.

The Buckrange sandstone (Upper Cretaceous) reservoir in the Stephens field was discovered June 8, 1922, at a depth of 2,082 feet. The initial daily production of the discovery well was 33 barrels of 29.3° API gravity oil. Over 300 wells have been drilled in the field, and of these approximately 200 have been abandoned. Almost 9,000,000 barrels of oil has been produced, and it has been estimated that 100,000,000 barrels of oil remains in the reservoir.

The amount of gas initially in solution is unknown, but it undoubtedly was small as gas production from the field has been low. The Buckrange sandstone reservoir does not appear to have a water table in the Stephens field. Core analyses and electrical log interpretations thus far indicate that the Buckrange formation is composed of sandstone and sandy shale and averages less than 10 feet in thickness. The oil-productive part of the formation is shown on electrical logs as two continuous layers of sandstone separated by 2 to 4 feet of shale or hard limey siltstone. The sandstone is fine to medium-coarse grained and sometimes contains fine flakes of mica and argillaceous material. The limited flood-pot data now available indicate that the main part of the sand will take water and oil can be flushed out at reasonable pressures.

Chemical Characteristics of Waters From the Canyon, Strawn, and Wolfcamp Formations in Scurry, Kent, Borden, and Howard Counties, Tex.

A report[3] containing information relative to the oil-field brines from the Scurry Reef formation in Scurry and adjacent counties of West Texas was published in June 1953. Results of water analyses of samples obtained from 67 wells were tabulated, and the chemical characteristics of the different formation waters were determined and were compared using graphical illustrations and contour maps. Limited information indicated that the formation waters in the area may be distinguished by certain chemical characteristics and that these characteristics may vary for a particular formation water within the Scurry Reef area from one part of the area to another.

Information derived from studies of water analyses is used to solve many problems involving (1) producing equipment subjected to corroding and scaling tendencies of oil-field brines, (2) pressure-maintenance programs where water is the injected medium, (3) formation correlation, (4) detection of well leaks, and (5) identification of water sources.

Effects of Separator Pressures and Temperatures on Gas-Oil Ratio Measurements, Scurry Reef Field, Scurry County, Tex.

Operating temperatures and pressures of separators were found to vary to a large extent from one tank battery to another in Scurry County, Tex., during the Bureau well testing in the Scurry Reef field. The effects of these pressure and temperature variations on production data were determined so that the data obtained from 45 well tests could be converted to a common base for comparisons.

The effects on production owing to variations in separator temperatures were determined by making a series of four tests on a well centrally located in the field. The separator temperature, during a series of tests in which the separator pressure was maintained essentially constant at 40 p.s.i., was varied from 68.5° to 133.0° F. by controlling the temperature of the fluid entering the separator with a thermostatically controlled heat exchanger.

The effects of variation in separator pressures on resulting production data were determined in the laboratory. A series of 4 flash-gas liberation experiments as conducted to simulate field producing conditions when the separator temperature was 60° F. The separator pressure in the laboratory was varied, from one test to another, from 0 to 214 p.s.i.

An operating separator temperature of 60° F. and a pressure of 40 p.s.i. were selected arbitrarily as a common base for comparing well-test data. Curves were constructed showing correction factors for converting all well-test data to this base (see figs. 1 and 2). An example of the use of these curves follows: The measured gas-oil ratio during a well test was 1,000 cubic feet per barrel when the average separator temperature was 87° F. and the average separator pressure was 28 p.s.i., and it was desirable to know what the ratio would have been if the separator temperature and pressure had been 60° F. and 40 p.s.i., respectively. Reference to figure 1 shows a conversion multiplier of 0.90 for a separator temperature of 87° F., and figure 2 shows a conversion multiplier of 0.95 for a separator pressure of 28 p.s.i. Therefore, the corrected gas-oil ratio would be 1,000 x 0.90 x 0.95, or 855 cubic feet per barrel.

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[3] Elliott, W. C., Jr., Chemical Characteristics of Waters From the Canyon, Strawn, and Wolfcamp Formations in Scurry, Kent, Borden, and Howard Counties, Tex.: Petrol. Eng., vol. 25, No. 6, June 1953, pp. B77-B80, B83, B85, B88, B89.

This study showed that normal variations in both separator temperatures and pressures materially influenced gas-oil ratios, specific gravities of separator gas, formation volume factors, and A.P.I. gravities of stock-tank oil in the Scurry Reef field. Similar influences in other fields may be caused by normal variations in separator temperatures and pressures. Accordingly, a manuscript is in preparation for trade journal publication showing this information.

Study of Reservoir-Oil Samples

Effects of Injected Gas Upon Reservoir Oil Characteristics

Data obtained from laboratory analyses of subsurface oil samples collected in 1937, 1941, 1947, and 1948 from wells producing from the Basal Sundance sand, Lance Creek oil field, Wyo., have been studies in detail and are being consolidated into a report. The report will discuss the change that has occurred in the reservoir oil characteristics during the pressure-maintenance program of gas injection. The approximate increase in recovery of liquefied petroleum gases as a result of the vaporization of these hydrocarbon components of the gas in solution when the oil is contacted by the relatively dry injected gas has been determined.

The subsurface sample data have been used to determine a theoretical recovery for a solution-gas drive. Comparison of this theoretical recovery to the actual and estimated ultimate recovery at abandonment for the pressure-maintenance program provides an approximate evaluation of the increased recovery of oil that has been and may ultimately be obtained as a result of injecting gas back into the reservoir. Sample data are available that show the effects of injected surplus propane and butanes on the characteristics of oil in a particular area of the reservoir. Other sample data, from samples obtained 10 years apart from the same well, show that the processes of liberating gas in the reservoir with pressure decline and liberating gas during laboratory differential-gas-liberation analyses of samples are essentially the same. These findings are particularly valuable in that field data have not previously been available to substantiate the general belief that these processes of gas liberation are very similar. The results of this study are most significant to an understanding of what happens to the oil in a reservoir as production takes place, and they are therefore being prepared for publication.

Vaporization of Reservoir Oil by Cycling Gas

The objective of this laboratory research problem is to improve present accepted methods of calculating the benefits of pressure maintenance; thus fostering this oil-production practice, which is such an important factor in petroleum conservation. A study is in progress to determine the rate of vaporization as gas is cycled through an oil reservoir during a pressure-maintenance program. The successful completion of this study will permit reservoir engineers to make more accurate predictions of ultimate recovery of oil, natural gasoline, and LPG (liquefied petroleum gas) from reservoirs in which gas is being or is to be cycled. This should, in turn, result in wider usage of pressure maintenance, which will result in greater ultimate oil recoveries.

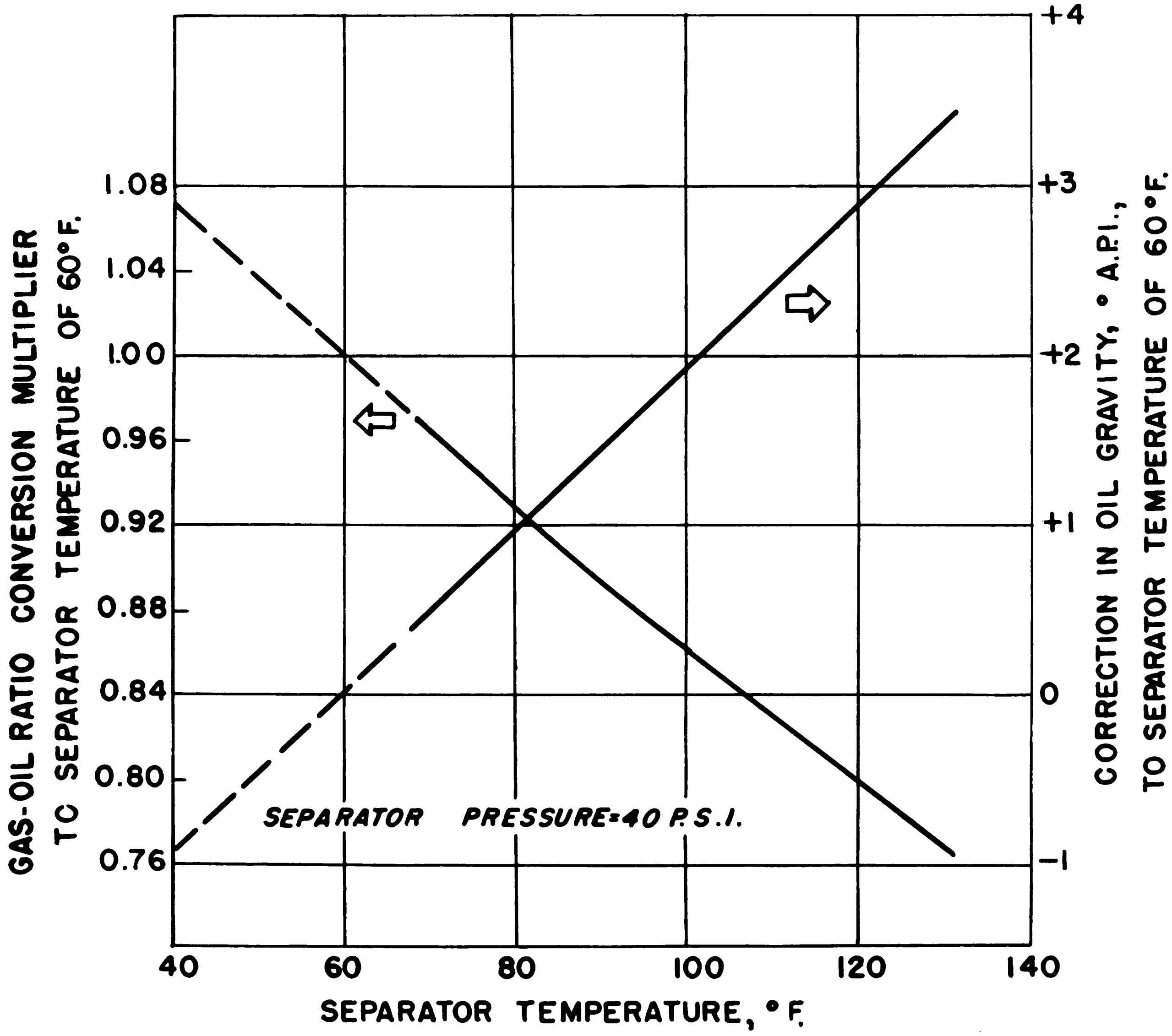

Figure 1. - Factors for converting well-test data to a base separator temperature of 60° F., Scurry County, Tex.

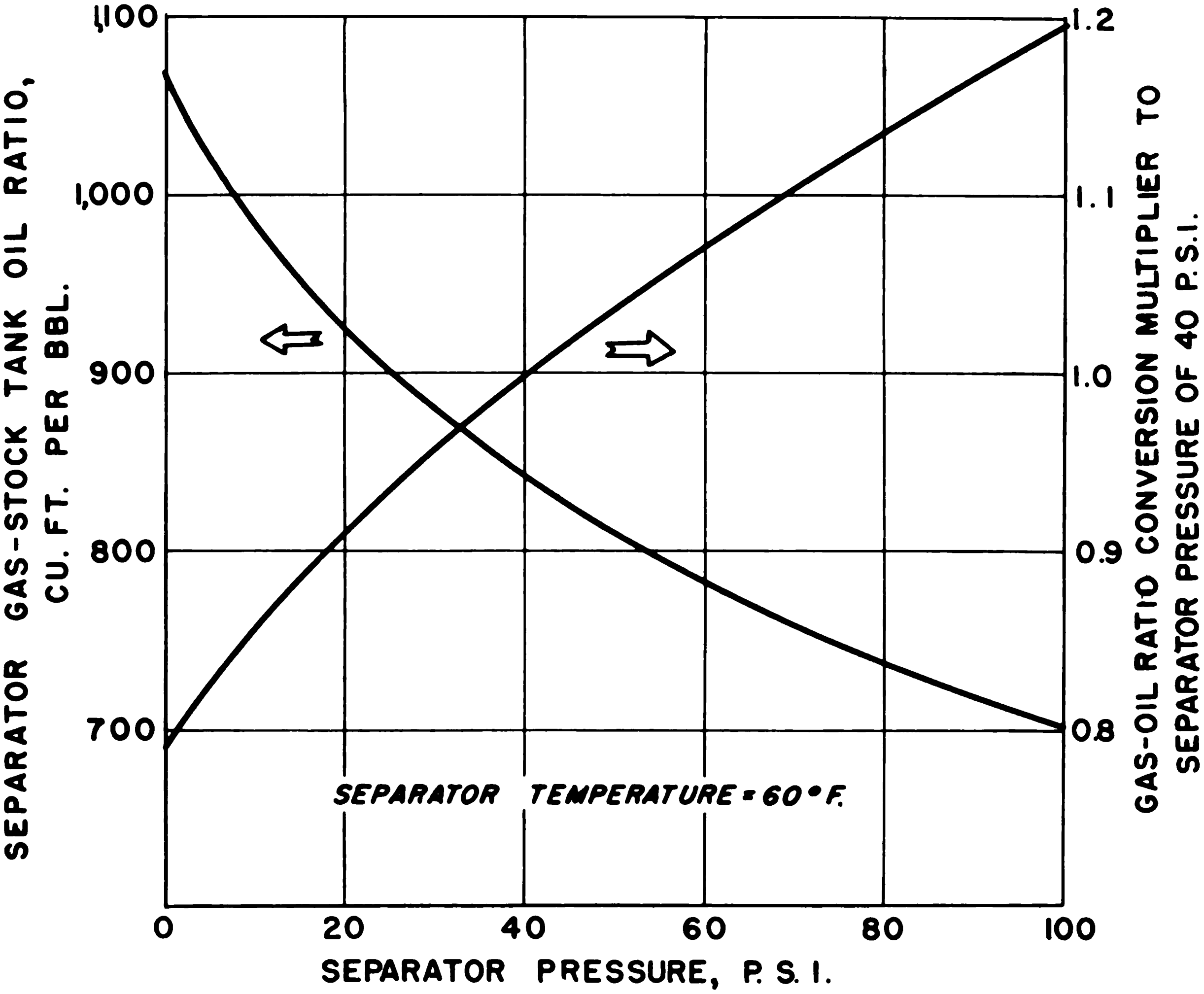

Figure 2. - Conversion factors for gas-oil ratios to base separator pressure of 40 p.s.i., Scurry Reef field, Scurry County, Tex.

The vaporization of oil that occurs as dry gas is cycled through an oil reservoir will be determined in the laboratory by passing known volumes of dry gas of known composition through a laboratory reservoir filled with an actual sample of reservoir oil. This reservoir consists of a sand-packed tube with valve outlets at each end. (A schematic drawing of the reservoir and auxiliary equipment is shown in fig. 3.) The pore volume of the reservoir has been determined, and thus the volume of reservoir oil that can be charged into the reservoir is known. Pressure-volume-temperature (P-V-T) properties and the composition of the reservoir oil will be determined before beginning an experiment. Thus, the amount of each light hydrocarbon fraction in the oil charged into the reservoir at the beginning of an experiment can be calculated. The composition and volume of the gas that will be forced through the reservoir, together with composition and volumes of both liquid and gas phases produced from the reservoir, will be determined. A balance can be made at any time during an experiment between (1) the composition and volume of the fluid produced in both the liquid and gas phase, (2) the composition and volume of gas injected into the reservoir, and (3) the composition and volume of the fluid in the reservoir. Thus, both the amount of oil vaporization that occurs and the composition and volume of the oil remaining in the reservoir can be calculated.

The laboratory equipment now is believed to be perfected to the point where actual tests using reservoir oil can be conducted successfully. The first tests will be made by passing dry natural gas from the city distribution system through the reservoir after it has been filled with reservoir oil from the Scurry Reef field, Scurry County, Tex. As composition of this gas must be known and as the composition of the natural gas may vary from day to day, it is desirable to store enough gas to last for several years so that a separate analysis of the gas will not be necessary for each experiment. Gas has been compressed into 2 large steel pressure vessels to 1,140 p.s.i., and the composition of this gas has been determined. Samples of reservoir oil are on hand and the pressure-volume-temperature properties and the composition of the oil have been determined.

Characteristics of Gas-Condensate Fluids

The results of experimental research on the specific volumes and phase states of natural gas and gas-condensate fluids have been correlated to provide compressibility and phase diagrams that will indicate the properties of these fluids when only the composition is known. A total of 610 figures and tables have been prepared for the manuscript of a monograph planned to serve as a reference book for the production engineer. When completed under the title Phase Relations of Gas-Condensate Fluids the monograph will show correlations for two-component and similar simple systems as well as for the complex multicomponent systems with which the natural-gas and petroleum industry is concerned. Although a substantial amount of experimental data will be presented for the first time, the principal purpose of the manuscript is to present correlations of all pertinent data available and to show by detailed examples how the correlations are to be applied to practical problems. Applications pertaining to the compressibility of fluids at reservoir and pipeline pressures and temperatures and to the phase-boundary-state properties and phase diagrams of two-component and multicomponent mixtures will be included. This kind of approach should be of great help in solving problems pertaining to reserve estimates and to the determination of the recovery procedure for maximum economic benefits. In particular, information has been given that will aid in determining early in the life of a field whether gas should be returned to the reservoir and whether the fluid in the reservoir should be recovered as if it were gas-condensate fluid or crude oil.

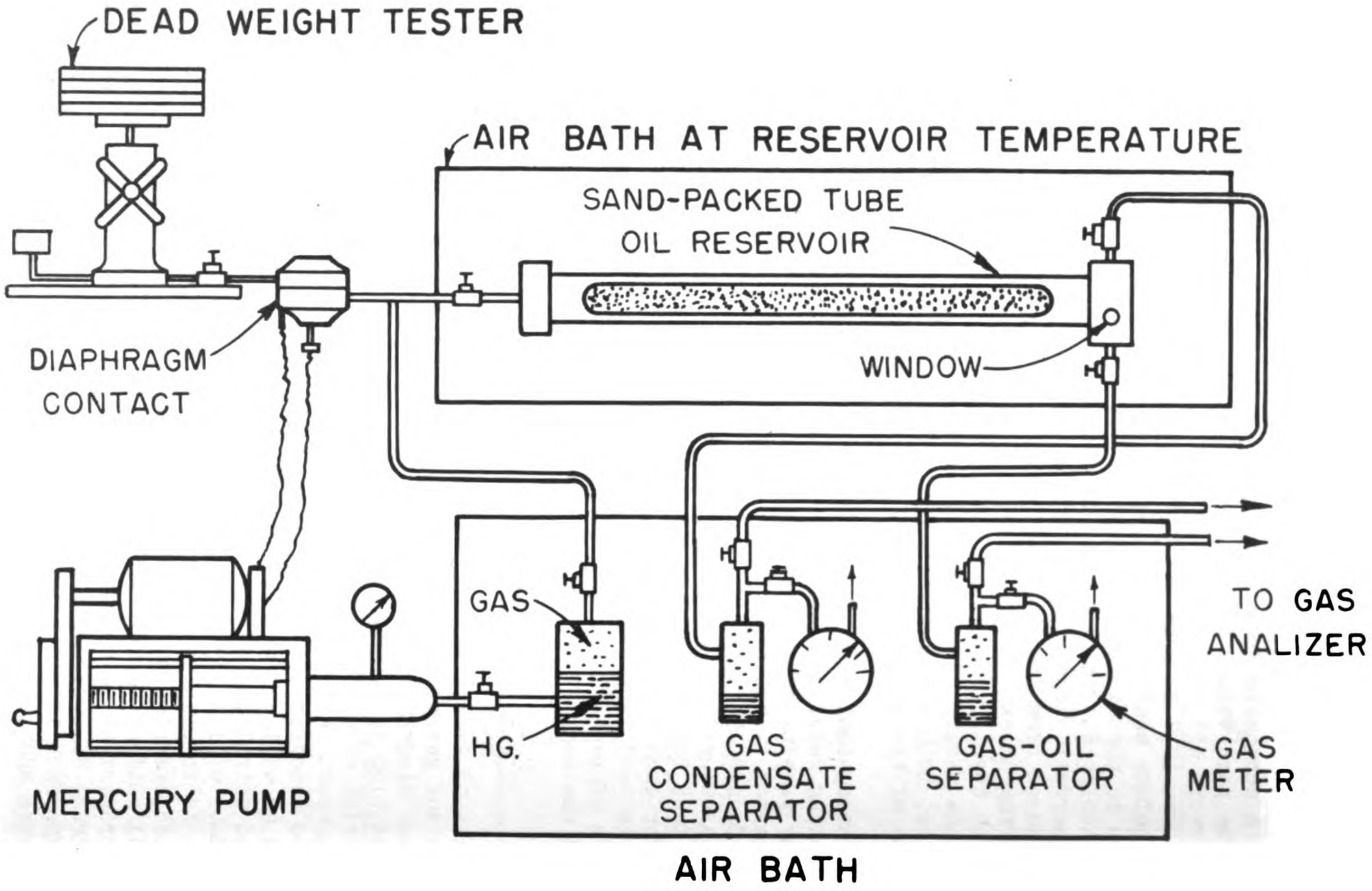

Figure 3. - Schematic drawing of equipment for determining oil evaporation during gas cycling.

Correlation of the phase diagrams of gas-condensate fluids with composition involved an investigation of the properties of components and of two- and three-component mixtures. To find a means of estimating the maximum dew-point pressure on the phase boundary of a complex fluid, it first was necessary to find a correlation between the composition and the critical and cricondenbar states of two-component mixtures. Both pressures and temperatures were studied. On the basis of the findings, coordinate units were determined for the phase diagrams that permitted accurate correlation of phase-diagram characteristics with composition, and means were found for determining the change that would occur in the phase diagram of a fluid with a given change in composition.

One of the basic correlations - the relationship between composition and the critical pressure of two-component mixtures - is illustrated in figure 4. The ordinate of the chart is the ratio of the actual critical pressure to the molal average critical pressure. The abscissa or composition variable is the difference in normal boiling points of the two components divided by the molal average absolute boiling point of the mixture. Any one of the solid curves in the figure shows pressure-composition relationships for mixtures containing the indicated mole fraction n'_L of the lighter of the two components. As the ratio, B_H/B_L, of the absolute boiling point of the heavier component to the absolute boiling point of the lighter component increases, the ratio of actual critical pressure to molal average critical pressure increases. The more the two paraffin components differ in their properties, the more the critical pressure of their mixtures will exceed the average critical pressure of the components. Dashed curves in the figure trace the locus of constant values of the boiling-point ratio and show how the critical pressure of a mixture of two given components will change with the relative amounts of the components in the mixture.

This correlation of critical pressure data on 18 two-component mixtures fitted the data used in preparing the correlation with an average uncertainty of only 2.4 percent. The 10 percent of the experimental data varying the most from the correlation curves is subject to an average error of 6.8 percent. The correlation can be useful for predicting the critical pressure of two-component paraffin mixtures other than those on which experimental investigations have been made, but it was especially useful for testing the applicability of the correlating function and as a step in the development of other correlations pertaining to the phase relations of natural gas and gas-condensate fluids.

Productivity of High-Pressure Oil and Gas Wells

As a part of the research on the productivity of oil and gas wells, Bureau of Mines engineers have completed a study of the flow of natural gas in the producing strings of gas wells. Previous work to increase the accuracy of subsurface-pressure gages permitted a field study to determine friction factors[4] for gas wells. Friction factors were determined by tests on wells in six fields in Texas, Oklahoma, and Louisiana. Data were collected on 17 gas wells with flow strings of 1-1/4-, 2-2-1/2-, and 3-inch tubing and 5-1/2- and 7-inch casing and on flow in the annular space between the tubing and casing of 4 wells. A manuscript entitled "Friction Factors for Measuring the Productivity of Gas Wells" now nearing completion, will summarize the experimental work on friction factors for tubing and casing of gas

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[4] As used in this report, the term "friction factor" indicates 1/f where f is the friction coefficient commonly used in flow equations. However, several writers have used the terms "friction factor" and "friction coefficient" interchangeably. This practice has not been followed in this report.

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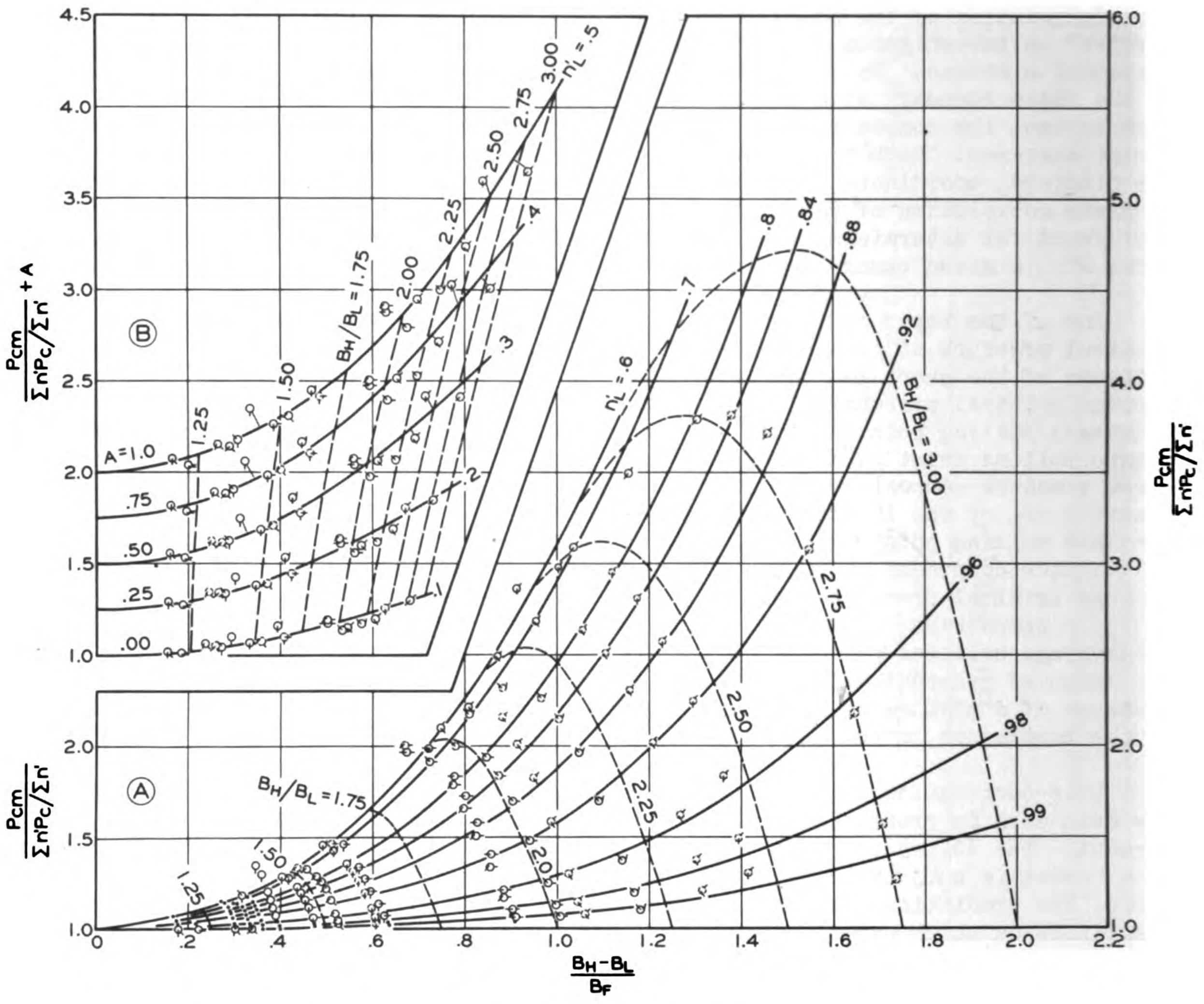

Figure 4. - Relationship of measured critical pressure and molal average critical pressure of two-component, hydrocarbon mixtures.

wells and will explain a method of correlation permitting the calculation of friction factors for a flow string of any size.

Although several means of correlation were attempted, flow tests on horizontal test pipes from the project Study of Flow of Natural Gas in High Reynolds Number Pipelines show that the Nikuradse[5/] resistance equation for flow in rough pipe provides the best means of correlating friction factors for the flow of natural gas through commercial pipes. Accordingly, the friction factors for the flow strings of gas wells were correlated by an average absolute roughness value computed by the Nikuradse rough-pipe equation.

The average absolute roughness of all the data for the flow strings of gas wells was 0.000,65 inch. The use of this average absolute roughness with the Nikuradse rough-pipe equation to calculate friction factors for the various sizes of tubing and casing is illustrated in figure 5. The diagonal line across the graph is developed from the resistance equation of Nikuradse[6/] for turbulent flow in smooth pipes. Also, figure 5 illustrates the region at the lower Reynolds numbers where the roughness of the pipe ceases to have an effect on the friction factor, and the friction factor and the flow characteristics become identical with that for a smooth pipe.

The use of the average absolute roughness value in the rough-pipe equation with certain restrictions on the range of Reynolds number will permit estimation of friction factors for all sizes of flow strings commonly used in gas wells. It is to be stressed that an average absolute roughness value does not apply equally to all flow strings in gas wells because the flow strings of some wells may have been exposed to corrosive conditions and the flow strings of other wells may be coated on the inside with drilling mud or cement. However, the absolute roughness value of 0.000,65 inch will give friction factors that are more representative of gas-well conditions than those in common use today.

This research on the productivity of high-pressure oil and gas wells is being conducted in cooperation with the American Gas Association.

Productivity of Wells and Reservoir Performance

A study has been made and a report[7/] completed concerning the magnitude of the amount of supersaturation that occurs in an underground reservoir during the flow of oil and gas to wells and of the amount of undersaturation that occurs during repressuring of an oil reservoir.

Many petroleum engineers and research investigators believe that the oil and gas in partly depleted solution-gas drive reservoirs are not in equilibrium. Part of the reason for this belief stems from the fact that, in determining pressure-volume-temperature data in the laboratory, the oil and gas must be thoroughly

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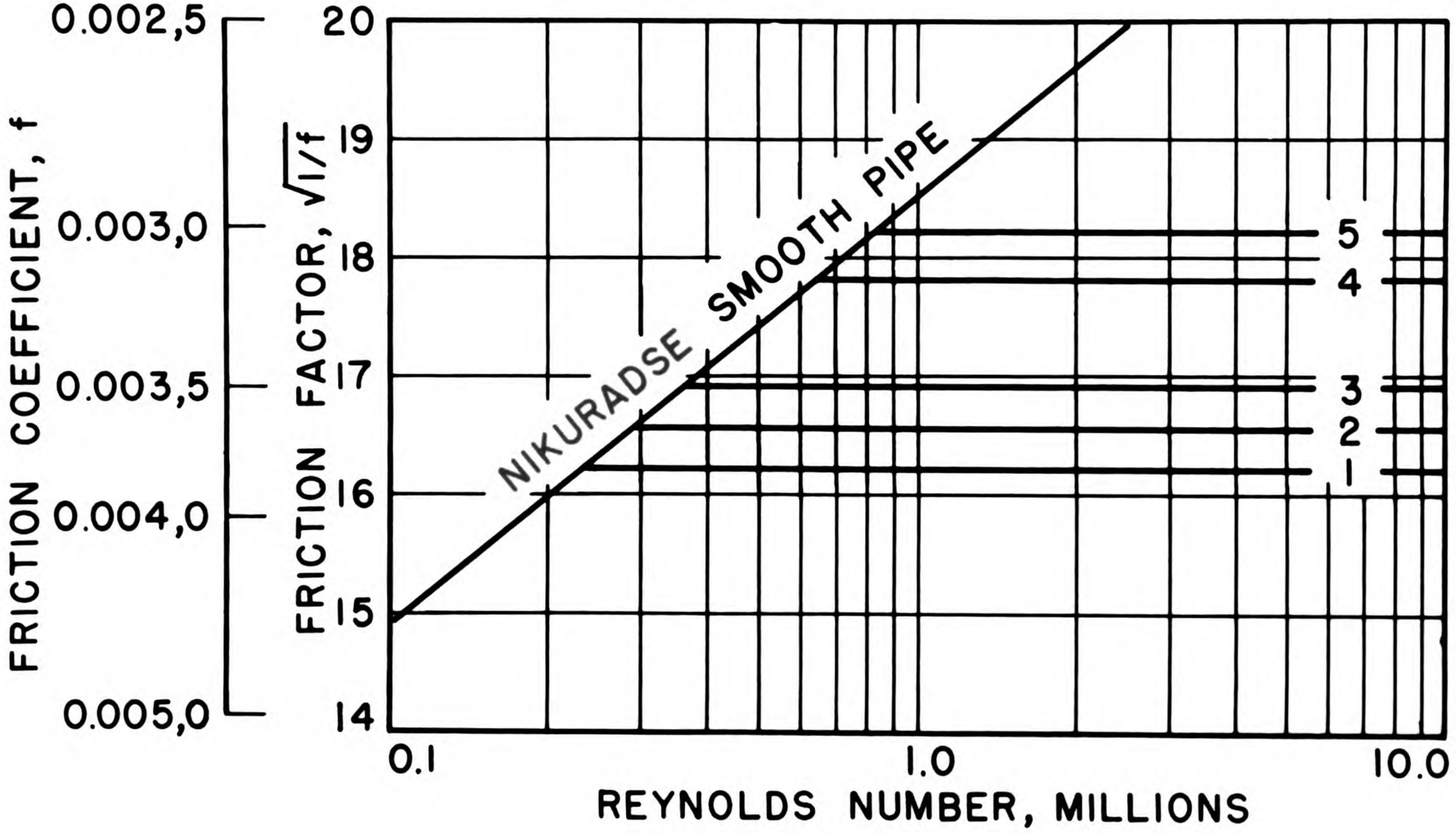
[5/] Nikuradse, J., Stromungsgesetze in Rauhen Rohren: V.D.I. Forschungsheft 361, 1933; translation, Laws of Fluid Flow in Rough Pipe: Petrol. Eng., vol. 11, 1940, pt. 1 March, pp. 164-166; pt. 2 May, pp. 75-82; pt. 3 June, pp. 124-130; pt. 4 July, pp. 38-42; pt. 5 August, pp. 83-87.

[6/] Nikuradse, J., Gesetzmassigkeiten der Turbulenten Stromung in Glatten Rohren. V.D.I. Forschungsheft 356, 1932.

[7/] Higgins, R. V., Study of Undersaturation During Repressuring and Supersaturation During Flow of Oil to Wells. Pres. at AIME fall meeting, October 1953.



1. 2-INCH TUBING, I.D. = 1.995 IN.
2. 2 1/2-INCH TUBING, I.D. = 2.441 IN.
3. 3-INCH TUBING, I.D. = 2.992 IN.
4. 5 1/2-INCH CASING, 14 LB., I.D. = 5.012 IN.
5. 7-INCH CASING, 24 LB., I.D. = 6.336 IN.

Figure 5. - Friction factors for circular flow strings computed with the Nikuradse rough pipe equation; absolute roughness = 0.000,65 in.

agitated in the P-V-T cell to bring about phase equilibrium as the rate of diffusion of gas in oil is otherwise too slow. On the other hand, no agitation occurs in an underground reservoir. Accordingly, if nonequilibrium conditions exist in a reservoir, correction factors to P-V-T data determined in the laboratory would be required for material balance calculations and for the phase and viscosity relations in relative permeability and in other flow work.

The study is based on earlier laboratory findings of other investigators on the rate of diffusion of gas in oil as a function of the depth of oil. Utilizing those relationships and the principles of reservoir mechanics, a quantitative estimate of undersaturation and supersaturation was calculated. The results showed that the diffusion of the gas is rapid enough so that for all practical purposes no supersaturation exists during the flow of oil to wells or undersaturation during repressuring in reservoir sands having some effective permeability to gas.

The reason diffusion of the gas keeps the oil virtually saturated is attributed to the long time required in radial flow for oil to reach the well and the slow rate at which the pressure in reservoirs is increased during repressuring.

Developments in oil-reservoir engineering in recent years indicate the need for further research on the fundamental behavior of two-phase fluids in porous mediums. Little attention in this respect has been given to the transfer of heat through the rocks and fluids of oil-reservoir systems. A Bureau engineer and an engineer at the University of California jointly have made a brief study of the conduction of heat incident to the flow of vaporizing fluids in thermally isolated columns of sand.

This theoretical study indicates that for the circumstances considered, heat-conductive effects arising from temperature gradients through porous rocks conveying one-component vaporizing fluids are negligible. Plans are made to publish the results of this study in an engineering journal.[8]

Recently theoretical work was undertaken to calculate for an idealized solution-gas-drive reservoir the liquid-oil saturation about a well at the time of the economic abandonment rate of oil flow. The purpose of this work is, first, to develop an appropriate method for calculating the liquid-oil saturation and, second, to determine how this distribution at the economic abandonment rate of flow affects estimates of oil reserves. Work has not yet progressed far enough on this study to report any results.

Well-Completion Methods

The objective of this research is the experimental determination of the effect of well-completion methods on the productivity of oil wells. The drilling of a well into the reservoir rock involves several operations that may reduce the ability of the reservoir rock to conduct fluids into the well bore. For example, water-base drilling muds may invade the reservoir rock causing the clay in the rock to swell and partly block the passages through the rock; also, cement may close the pores of the rock when casing is cemented. Conversely, acid may be used on limestone or explosives or hydraulic fracturing may be used on sandstone to open new channels or enlarge existing ones. The pressure-buildup method of testing an oil well permits evaluation of the extent to which the drilling and completion of a well has damaged or improved the permeability of the reservoir rock in the immediate vicinity of the well. The total effect of well completion on permeability of the reservoir rock has been termed "skin effect" by some investigators and "well-completion efficiency" by others.

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[8] Miller, F. G., and Seban, R. A., Conduction of Heat Incident to the Flow of Vaporizing Fluids in Porous Media.

The success of the pressure-buildup method of testing to determine the effect of well-completion methods on well productivity in the Scurry Reef field influenced Bureau of Mines engineers to undertake an evaluation of completion practices in the Spraberry area of West Texas. Since the beginning of the test work in December 1952 in the Spraberry area, a total of 14 pressure-buildup tests were conducted on 13 wells, of which 6 were producing from the Upper Spraberry reservoir and 7 were producing from the Lower Spraberry. Two pressure-buildup tests were conducted on one well; the first was before and the second was immediately after an attempt was made by the operator to restimulate the well by fracture treatment.

The results of the tests showed that the permeability of the reservoir rock for 13 wells ranged from 0.9 to 19 millidarcys, and only 1 well of the 13 wells tested showed that the flow capacity of the reservoir rock was reduced near the well bore. Published information on core samples of the reservoir rock from 64 wells in the Spraberry area show an average permeability of 0.3 millidarcy for the matrix rock. The pressure-buildup tests by Bureau of Mines engineers indicate that the permeability of the matrix rock ranged from 0.9 to 19 millidarcys. The excess permeability is caused by the extensive fracture system in the reservoir rock, which does not influence the permeability determined by core analyses.

The information developed on the effect of well-completion practices on the productivity of wells in the Spraberry area will be published in the near future. However, at least one more well will be tested before the study of the Spraberry area will be completed.

The study of well-completion practices was continued in California also and pressure-buildup data from selected wells in a deep field in the San Joaquin Valley were analyzed to develop information on the effect of completion fluids on the permeability of oil-bearing formations to the flow of oil.

The preliminary results of these studies indicate that it is possible to calculate the permeability to oil of a producing formation from the rate at which the pressure builds up to static conditions in a producing well after it is shut in. The rate of pressure buildup is controlled by the resistance of the formation, the viscosity of the reservoir fluid, and the permeability of the formation around the well bore resulting from the invasion of drilling fluid during completion.

An analysis of pressure-buildup data for a number of wells in which water-base and oil-base completion fluids were used shows conclusively the detrimental effect of invasion of filtrates from water-base drilling fluids on the permeability of the producing formation.

Well histories show that efficient completion practice rewards the operator by extending the flowing life of wells and increasing their productivity and ultimate recovery.

Well-Spacing Studies

An extensive study of multiphase flow and the problem of spacing oil wells has been completed. The results of this work have been published.[9] Primary objectives of this project were to promote a greater range of understanding of the well-spacing problem, to show and explain the barriers to incontrovertible physical solutions (as contrasted to purely economic solutions), to indicate how the problem rests on the incomplete, expanding foundation of reservoir engineering, and to coordinate its scientific and practical aspects in one report.

Mathematical and physical concepts pertaining to the static behavior and the flow behavior of mixtures of natural gas, crude oil, and water in porous rocks are discussed in the report, and the elements of Darcy's law in applications to multiphase flow are examined. Attention is given also to capillary phenomena and heat effects incident to fluid flow through porous mediums. Finally, practical considerations in the treatment of well spacing are discussed. The forthcoming bulletin is essentially a well-spacing and reservoir mechanics text.

Drilling-Fluid Research

Determination of Water Content of Oil-bearing Rocks

Work was continued on the correlation of the water contents of oil-base core samples as determined by distillation with water saturations determined by (1) capillary displacement of interstitial water by air, (2) displacement of air from a clean extracted core by mercury, (3) evaporation of liquid from the pore space of a core sample, and (4) centrifuging liquid from the pore space of a core sample. Several discrepancies in the water contents obtained by these methods have been noted when the results are compared with the water contents obtained by the distillation method. Accordingly, it has been deemed advisable to correlate these methods of obtaining the water contents of cores with one another, using the distillation method as a criterion for judging the relative accuracy of the other four methods.

Quebracho Substitutes

A manuscript[10] has been completed presenting the results of a study to determine the relative merits and quantitative availability of various substitutes for quebracho for controlling the viscosity and filter properties of clay-water drilling muds. It will be published as a trade journal article in fiscal year 1954.

The search for quebracho substitutes was undertaken at the suggestion of the Munitions Board in cooperation with the Regional Research Laboratories of the Department of Agriculture and many industrial firms to explore the possibilities of providing an adequate replacement material in an emergency that would cut off or drastically reduce importations of quebracho from South America.

Some 75 materials comprising natural and synthetic substances were tested. Most of the natural materials were agricultural and wood byproducts and most of the

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[9] Miller, F. G., Multiphase Flow Theory and the Problem of Spacing Oil Wells: Bureau of Mines Bull. 529, 1954, 35 pp.

[10] Caraway, W. H.; Domestic Substitutes for Quebracho in Oilwell Drilling Fluids: Petrol. Eng., vol. 25, No. 12, November 1953, pp. B-81 - B-89.

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synthetic materials were detergents. Although none of the materials tested was found to be equivalent to quebracho in effectiveness, especially on a pound-for-pound basis, some materials approached quebracho in controlling the properties of three native clay drilling fluids under most conditions. The paper presents the results of laboratory evaluation tests showing the relative merits of 15 substitute materials as to their effect on the viscosity and filter properties of these drilling fluids, their resistance to sodium chloride contamination, and their resistance to high-temperature deterioration. These 15 products were selected as the most promising of the 75 materials tested. In addition, the paper includes graphical data showing the comparative effectiveness of those materials that are believed to be of the most practical interest. Included also is a discussion of the availability of some of the more effective substitutes.

One interesting byproduct material found to be effective in treating drilling muds is wine pomace, the residue that remains after pressing the juice from grapes. About 60,000 tons per year are available at 1 to 2 cents per pound.

A supplementary report also is being prepared on the auxiliary use of two substitute materials with quebracho to increase the resistance of drilling fluids to excessive salt contamination.

Clay Studies

Clay studies relating to the composition and control of clay-water drilling fluids has long occupied a prominent place in the primary production program of the San Francisco laboratory. In recent years the importance of the effect of naturally occurring clays on the flow of oil through reservoir sands and on the displacement of oil by water in secondary-recovery operations has become increasingly recognized by the petroleum industry, and an expanded program of clay research for the purpose of identifying clay minerals in oil reservoir rocks has been initiated. By identifying the types of clays found in oil well cores, it is possible to determine whether the reservoir sands may be damaged by water from drilling fluids or by water used in flooding. Knowledge of the characteristics of clays also is an aid in controlling the properties of drilling fluids.

Apparatus for identifying clay minerals by differential thermal analysis is being assembled.

In July 1952 the First National Conference on Clays and Clay Technology was held in Berkeley, Calif., under the sponsorship of the Bureau of Mines, University of California, California State Division of Mines, Federal Bureau of Reclamation, and other agencies and societies. Outstanding speakers from the United States and other parts of the world were obtained to discuss the many phases of the science of clay minerals. One whole day was devoted to the function of clay minerals in the petroleum industry. Papers presented at the conference together with the discussions will be published by the California State Division of Mines.

SECONDARY RECOVERY

Field Studies

Healdton Field, Okla.

Following completion of a petroleum-engineering study of the Healdton oil field, Carter County, Okla., 3 papers[11,12,13] on this work were published and 2 talks[14,15] were presented at meetings of technical societies. A summary of pertinent data regarding the field is given in table 1. The Healdton field was discovered in 1913, and by 1951 more than 2,600 wells had been drilled, of which 1,863 were still producing. By January 1, 1951, more than 211 million barrels of oil (see fig. 6) had been recovered from the Healdton sands in this field. Oil recovery from the 7,142 productive acres averaged 29,700 barrels per acre and 410 barrels per acre foot. Approximately 20 million of the 211 million barrels may be attributed to infill drilling, vacuum application, and gas injection.

The completion of additional wells during 3 infill drilling campaigns in 1926, 1936, and 1947 increased the rate of oil production from many leases and from the field as a whole (see fig. 6). The application of vacuum has been general in the field since 1938. Air and gas injection to increase oil production or to store gas for future use has been tried on a limited scale but without much increased oil production. To January 1951, recovery from 9 such projects, resulting from gas injection, totaled 295,000 barrels of oil.

Oil production is obtained from discontinuous and lenticular sands of late Pennsylvanian age, which range in depth from 700 to 1,400 feet. In general, the sands are highly porous and permeable with comparatively high oil saturation. In this study the Healdton sands were considered as belonging to four zones, the uppermost of which is called the Healdton First Sand and the lowermost the Healdton Fourth Sand. The first sand, now most nearly depleted, is the thickest and most extensive and should lend itself best to water-flood development. The second and third sands are extremely lenticular with alternating beds of sand and limestone of high and low permeability. The fourth sand covers a relatively smaller productive area and is more uniform in character but differs from the other sands in that natural water drive is the important production mechanism. The history of the natural water drive in the fourth sand for the field, and for certain representative leases shows that natural water flooding has been comparatively efficient in flushing oil from the sands and moving it to the producing wells.

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[11] Riggs, C. H., Wey, J. E., Sanabria, Edward, Jr., Meadows, Paul, Smith. W. C., and West, J. A., Petrol. Eng. Study of the Healdton Oil Field, Carter County, Okla.: Bureau of Mines Rept. of Investigations 4917, 1953, 76 pp.

[12] Riggs, C. H., and Wey, J. E., Millions of Barrels More Oil for Healdton Field: Oil Gas Jour., vol. 52, No. 6, June 15, 1953, pp. 96-100, 131-2, 134, 137, 140.

[13] Riggs, C. H., and Wey, J. E., Healdton Has Big Water-Flood Potential: World Oil, vol. 137, No. 1, July 1953, pp. 190, 192, 194, 196.

[14] Riggs, C. H., Secondary Recovery in the Healdton Oil Field: Pres. AIME Mid-continent Section Study Group, Tulsa, Okla., Mar. 24, 1953.

[15] Riggs, C. H., Healdton Oil Field, Past and Future: Ardmore, Okla., Geol. Soc., Ardmore, June 11, 1953.

TABLE 1. - Field and reservoir data, Healdton sands, Healdton oil field, Carter County, Okla.

General

Date of discovery		Aug. 14, 1913
Depth of wells	ft.	700 to 1,400
Total productive area	acres	7,142
Total wells drilled to Nov. 1, 1951		2,590
Wells producing as of Nov. 1, 1951		1,863
Stock tank gravity of oil	A.P.I.	26 to 35
Viscosity of typical stock tank oil of 31° A.P.I. at 80° F.	Cps.	13.3

Reservoir data

Average effective thickness	ft.	72
Average porosity	percent	21.6
Average permeability	md.	330
Average connate water content	percent	18.2
Average original reservoir pressure (est.)	p.s.i.g.	270
Average formation temperature (est.)	°F.	80
Gas in solution in reservoir oil per barrel of stock tank oil (est.)	cu. ft.	85
Formation volume factor (est.)		1.044
Original mobile oil reserves	bbl.	422,000,000
Total stock tank oil originally in reservoir	do.	674,195,000

Production data

Average initial oil production between 1913 and 1917, per well per day	do.	270
Maximum yearly oil production, 1917	do.	22,036,000
Yearly oil production, 1950	do.	2,263,000
Average daily oil production, 1950	do.	6,200
Average daily water production, 1950	do.	14,600
Average specific gravity of produced gas (est.)		0.88
Gasoline content of produced gas as of Jan. 1, 1951, per M cu. ft.	gal.	0.31 to 3.95

Recovery

Cumulative oil production to Jan. 1, 1951	bbl.	211,179,000
Oil recovery to Jan. 1, 1951, field average per acre	do.	29,570
Oil recovery to Jan. 1, 1951, field average per acre feet	do.	410

The study indicates that natural energy is now nearly exhausted and that many millions of barrels of oil will not be recovered by present operating methods. Flooding tests show that much of this oil can be flushed from the sands and forced to producing wells by water injected through specially equipped and properly spaced input wells. The introduction of water into the several sands and the control of its movements through the oil-bearing pore spaces between the sand grains will present many problems to the water-flood engineer. Careful consideration should be given to such factors as the distribution and continuity of sands, viscosity of the oil at formation temperature, oil and water saturation of the sand, and conditioning of injection water. Tests on samples of subsurface waters in the area indicate that

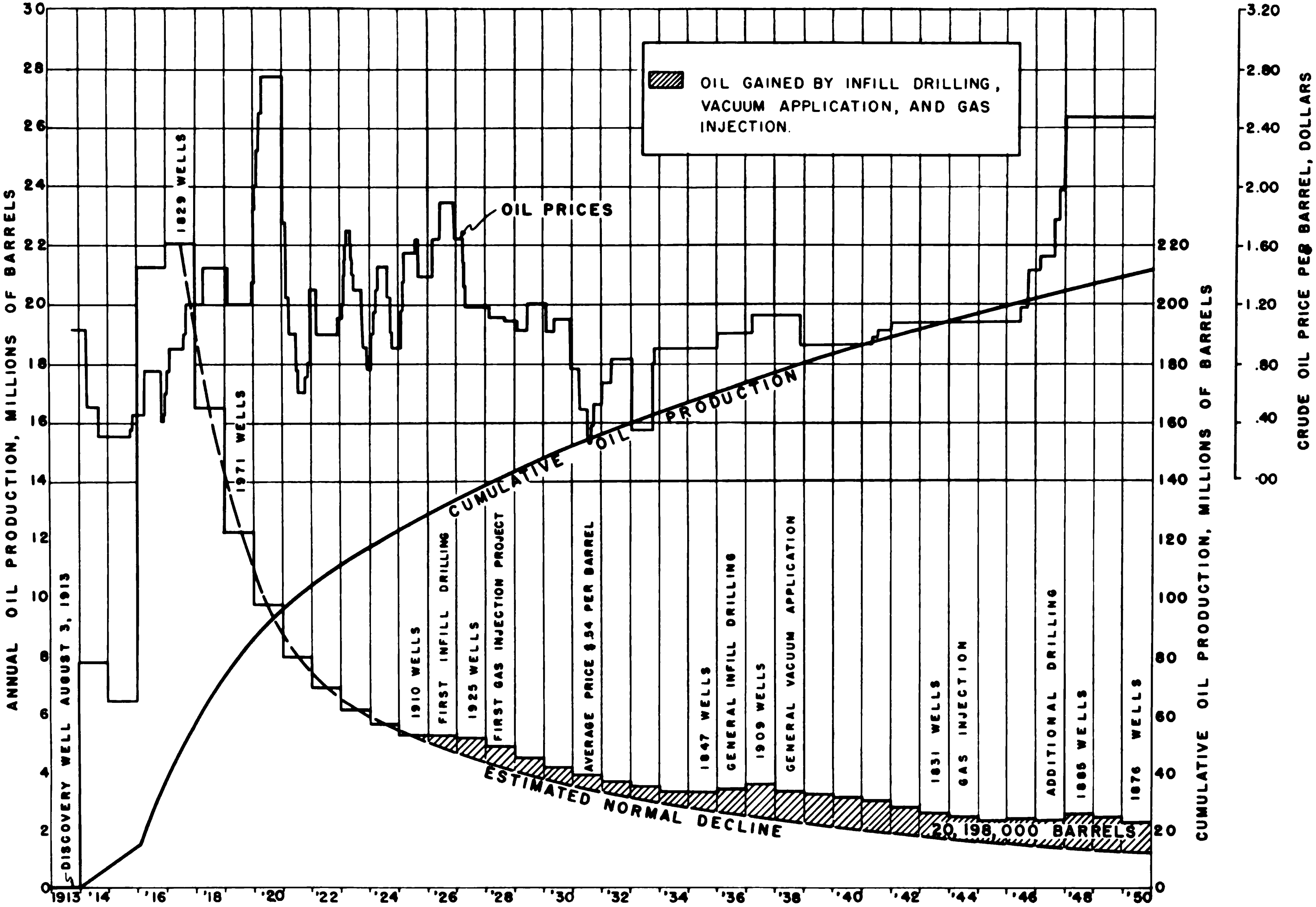

Figure 6. - Oil-production history and crude-oil prices (Healdton sand zone only), Healdton oil field, Carter County, Okla.

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if adequate volumes are available, these waters can be injected with only a small amount of chemical treatment.

Flat Rock Field

A report on the results of a petroleum-engineering study of the Flat Rock oil field in Osage County, Okla., is now being prepared for publication as a Bureau of Mines Report of Investigations. This field, discovered in 1904, had produced about 25-1/2 million barrels of oil by January 1953. Although 7 different horizons have been productive, about 22 million barrels of oil was recovered from the Bartlesville sand alone. Only this formation was studied in detail and considered for the application of secondary-recovery methods of production. The study shows that in 1952 the average daily oil and water production from the Bartlesville sand was 470 and 3,450 barrels, respectively. The individual production histories of several leases indicate a limited water drive in the Bartlesville sand in some parts of the field. Although most of the produced water is from the Bartlesville sand, a substantial part of it is extraneous water that is entering the formation through improperly cased or plugged wells or entering the well bore through leaking casing.

Of 66 leases in the field comprising 6,418 oil-productive acres, 19 leases, including 2,300 acres, are recommended for water-flood development. It is estimated that approximately 27 million barrels of oil could be recovered by efficient water flooding on these leases. Three water-flooding projects are now in operation, but only one of these shows promise of being a financial success.

Quapaw Field, Okla.

The Quapaw field in Osage County, Okla., is typical of many small fields in that area producing from the Bartlesville sandstone. As shown in figure 7 from a report by West,16/ the field was discovered in 1914, and the rate of oil production reached its peak (over 1-1/2 million barrels) in 1916 with approximately 110 active wells. Although the number of wells doubled during the next 4 years, the rate of oil production dropped approximately 65 percent because of the needless waste of reservoir energy. The application of vacuum began in 1920, and later the haphazard injection of air and gas greatly prolonged the economic life of the field, but by the end of 1951 many leases had been abandoned and there remained less than 100 active wells, which were producing about 50,000 barrels of oil yearly.

The cumulative total oil recovery to January 1952 from the Bartlesville sand of the Quapaw pool was 8,038,000 barrels. This is an average recovery of 2,614 barrels of oil per acre or 135 barrels per acre-foot of oil sand.

From the extensive study of available records on the Quapaw field, West concludes:

> Water flooding appears to be the only known method of production that can effect recovery of a substantial part of the oil remaining in the reservoir. It is believed that the reservoir is susceptible to water flooding, however, physical limitations will not permit displacement of all the mobile stock-tank oil in the reservoir by water flooding. It is estimated that 50 percent of the remaining mobile stock-tank oil can be recovered economically by efficient water flooding. This would provide a recoverable oil reserve, as of January 1, 1952 of approximately 8,000,000 barrels.

16/ West, J. A., Petroleum Engineering Study of the Quapaw Pool, Osage County, Okla.: Bureau of Mines Rept. of Investigations 4913, 1952, 39 pp.

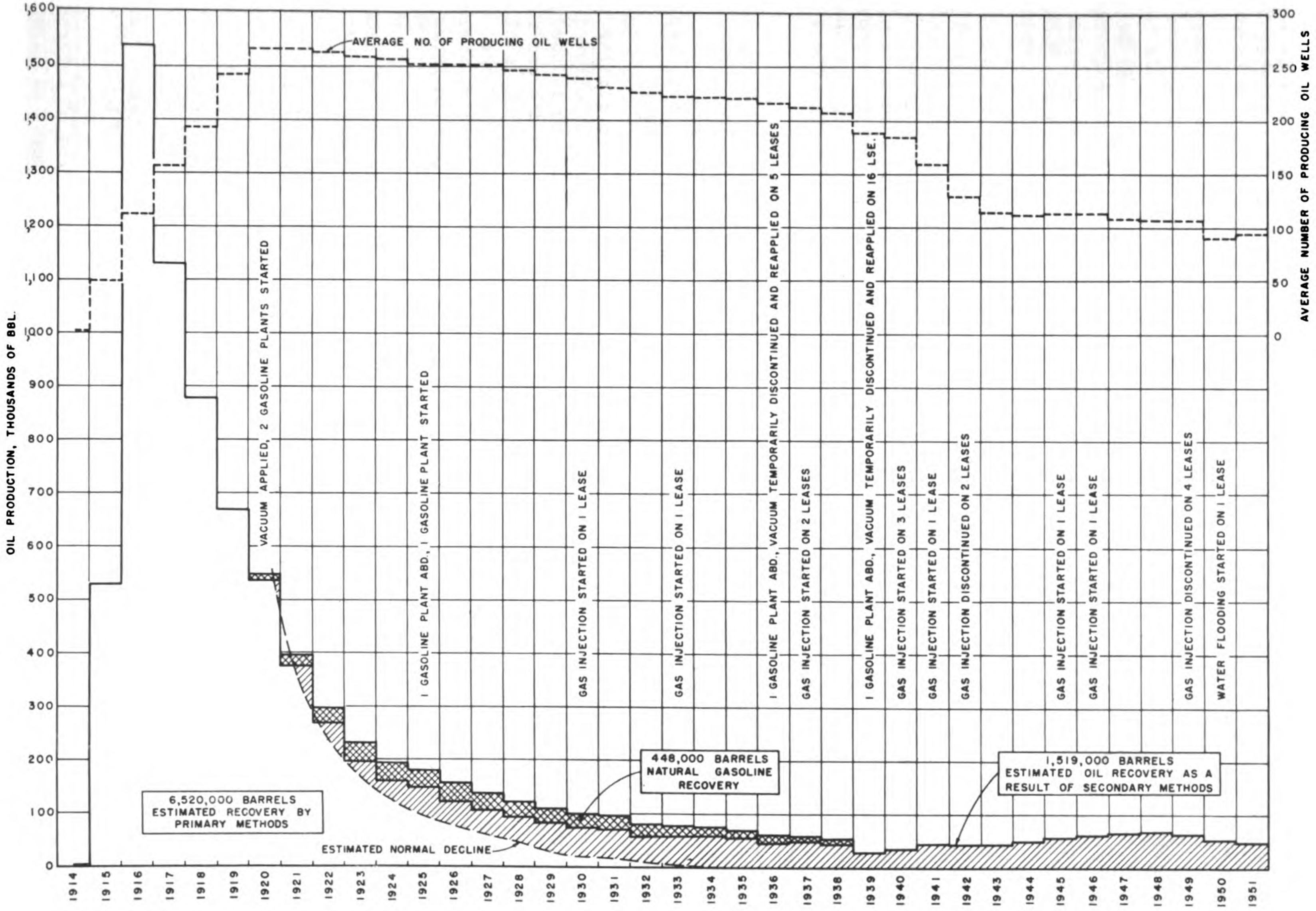

Figure 7. - Oil production, natural gasoline recovery, and average number of producing oil wells by years, Quapaw pool, Osage County, Okla.

Although the Quapaw field covers only about 3,000 productive acres it appears to represent many fields in eastern Osage County, Okla. If it proves feasible to recover 8 million barrels of oil from Quapaw by water flooding, as is indicated by West, it appears reasonable to expect the recovery of more than 100 million barrels of oil from the fields of this area by water flooding.

Water Flooding in Northeastern Kansas

A survey of water-flooding projects in northeastern Kansas was completed with the publication of a report[17] describing in detail each project in the area. The details of water-treating methods, the complete oil-production histories of each of the four counties in the area, and the results of water flooding are given. Maps of most of the major projects showing their status as of January 1, 1953, are presented also.

The practice of injecting water to stimulate oil production was legalized in Kansas in 1935, and the first water-flooding project authorized in the four-county area was initiated by The Texas Co. in December 1935 in Linn County. Forty-nine projects initiated in the area to January 1953 are estimated to have recovered approximately 10 million barrels of oil that would not have been produced by methods used before. About 7,900 productive acres had been, or are being, flooded by these projects. Approximately 136 million barrels of water had been injected in the 4-county area.

Oil production is principally from three formations, known locally as the Peru, Squirrel, and Bartlesville sandstones, of which the Squirrel is the chief source. All of the oil-producing formations are at depths of less than 1,000 feet. The sands being flooded are lenticular and have an average thickness of 25 feet, varying from 0 to 50 feet, with a few wells penetrating as much as 80 feet of sand.

The well-spacing patterns on the projects in the 4-county area are similar to those in other Midcontinent fields, with the exception of the variation followed in flooding shoestring fields where an elongated or modified 5-spot pattern is used. The wells in this pattern are spaced from 200 to 250 feet across the width and from 500 to 600 feet along the length of the field. In the very shallow fields, a close spacing ranging from 250 to 330 feet between like wells is used because of the limitation on pressure that can be applied without damage to the reservoir, whereas wider spacings ranging from 330 to 1,250 feet are used where the producing formations are at greater depths.

An adequate, reliable supply of suitable water is one of the major requirements for a successful water-flooding operation. The first few water-flooding projects in the area utilized fresh water from streams or ponds. Because of the unreliability of these sources of supply during dry seasons, wells were drilled on some projects to obtain brine from deep-seated aquifers when other supplies fail. Later, as the merits of brine became better known and the availability of a reliable supply from the Mississippi and Arbuckle limestones was established, many floods were begun with these aquifers as the principal source of supply. At the end of 1952 approximately 60 percent of the water-flooding projects depended wholly upon brine wells.

The release of the report on water-flooding projects in northeast Kansas was timed to coincide with the sixth annual tour of water-flooding projects by the

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[17] Powell, J. P., and Eakin, J. L., Water Flooding in the Oil Fields of Anderson, Franklin, Linn, and Miami Counties, Kans.: Bureau of Mines Rept. of Investigations 4991, 1953, 111 pp.

Kansas-Oklahoma Water Flooding Operators, the Northeast Oklahoma Oil Producers, Inc., and the Kansas Section of the American Institute of Mining and Metallurgical Engineers. The tour, participated in by 225 oil producers, petroleum engineers, and others interested in the broad subject of water flooding, covered the same area as that of the report. This is the fourth year that the tour has been arranged by Bureau of Mines engineers and timed to coincide with the release of a comprehensive Bureau of Mines report on the visited area. A public-address system was provided, and the information contained in the published report was supplemented by a discussion of each visited project by the project operator, the authors of the report, and selected engineers familiar with the respective floods.

North and West Central Texas

A preliminary investigation of the water-flooding activities of North and West Central Texas has continued during the year in cooperation with the North Texas Oil & Gas Association. Engineering data concerning the results obtained from water floods in the area were collected and compiled for 60 of the floods, or about one-third of those in the 22-county area. It is intended that these data be collected for all the water floods in the area and that they be maintained on a current basis for the purpose of preparing technical reports for publication. The technical reports will cover such subjects as: (1) Successful water floods in specific areas, (2) unsuccessful water floods emphasizing the reasons for their failure, (3) the results in general or in specific areas from water flooding particular formations, (4) water-treating facilities used by different operators on individual projects, or (5) generalized summary of the water-flooding activities, with reference to the success and failure of all types of projects.

Special Field Problems

Physical Studies of Petroleum Reservoirs

The small-diameter, well-bore caliper and the liquid-level gage, both designed and constructed at the Petroleum Experiment Station in Bartlesville, Okla., were used in field studies of water tracers being developed to detect channeling between water-input and oil-producing wells. The mechanical operation of both instruments was satisfactory. Limitations were observed, however, in the method of making water-injectivity profiles by plotting the rate of descent of a column of water displaced from the well at a constant bottom-hole pressure by injecting gas from the surface. The loss of the gas-displacing medium to highly permeable zones in the upper part of the open hole after the liquid level has dropped below them has been found to be so great that the capacity of the available portable compressor is inadequate at many wells to maintain the constant bottom-hole pressure required by the method. In some tests it has not been possible with this compressor to displace all of the liquid from the well even though there was a highly permeable zone at the bottom of the hole. Other methods of making water-injectivity profiles are being investigated.

A patent[18] was issued and assigned to the Government covering the design of the liquid-level gage. A report also is being prepared for publication describing the design and operation of the instrument. The liquid-level gage consists essentially of a thin-walled metal float, which rises in the instrument when the liquid level is reached and thus effects the flow of current from the surface by moving an

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[18] Taliaferro, D. B., McClung, C. F., and Mueller, F. G., Instrument for Locating the Liquid Level in Wells: U. S. Letters Patent 2,610,506, Sept. 16, 1952.

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arm across a series of contacts in the electric circuit. The extent of the rise of the float is indicated at the surface by the amount of electric current flowing through the circuit.

The small-diameter well caliper was further perfected during the year, and a patent application on the design has been prepared. The instrument has many novel features of design. It is unique in that it is only 1-3/4 inches in diameter, it is run on a single conductor armored cable, the calipering arms can be retracted, and it measures four radii independently. In addition to both instruments having unique features of design, they are novel as to size. They were designed especially for use in water-injection wells, many of which are completed with 2-inch tubing cemented in place. Both instruments have an outside diameter of 1-3/4 inches.

An exhibit was displayed at the International Petroleum Exposition in Tulsa, Okla., in May 1953, to demonstrate the use of the well-bore caliper in a simulated shot-hole in an oil sand. The exhibit, shown in figure 8, attracted much attention and comment because of the unique features of the instrument. Four organizations, including 1 major oil company, 2 instrument-manufacturing companies, and 1 well-service company, have applied for permission to manufacture and use or market the caliper.

Pressure Decline Rates of Water-Input Wells

Recently wide use has been made of pressure buildup curves in fields producing under primary methods to determine the reservoir pressure and the effective permeability of the reservoir rock. Work has been started to determine the possibility of applying pressure falloff curves on shut-in water-input wells in the same manner. The initial tests appear promising, and it is thought that this simple test may prove to be an important tool in the analysis of water-input-well performance. It is possible that occasional pressure falloff curves may give a rapid and accurate measure of the effective permeability and thereby a measure of the extent of channeling or of the plugging that has occurred at the sand face or in the pores of the rock because of inadequate or improper water treatment.

Conditioning Water for Subsurface Injection

A study of methods and equipment for conditioning water for water flooding in the Midcontinent area was concluded after the extensive testing of 24 plants, and the results were published in a Bureau of Mines Report of Investigations.[19] A condensed report[20] on the work was presented in one of the trade journals, and the results were presented orally at meetings of the North Texas Section of the American Institute of Mining and Metallurgical Engineers[21] and at the Sixth Oil Recovery Conference of the Texas Petroleum Research Committee.[22]

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[19] Watkins, J. W., Willett, F. R., Jr., and Arthur, C. E., Conditioning Water for Secondary Recovery in Midcontinent Oil Fields: Bureau of Mines Rept. of Investigations 4930, 1952, 86 pp.

[20] Watkins, J. W., Willett, F. R., Jr., and Arthur, C. E., Conditioning Water for Secondary Recovery: Petrol. Eng., vol. 25, No. 5, May 1953, pp. B56-61.

[21] Watkins, J. W., Analysis of Water-Conditioning Methods Used in Midcontinent Oil Fields: Pres. North Texas Section AIME, Wichita Falls, Tex., Mar. 27, 1953.

[22] Watkins, J. W., Analysis of Water-Conditioning Methods Used in Midcontinent Oil Fields: Pres. Sixth Oil Recovery Conf. of the Texas Petroleum Research Committee, College Station, Tex., Apr. 23, 1953.

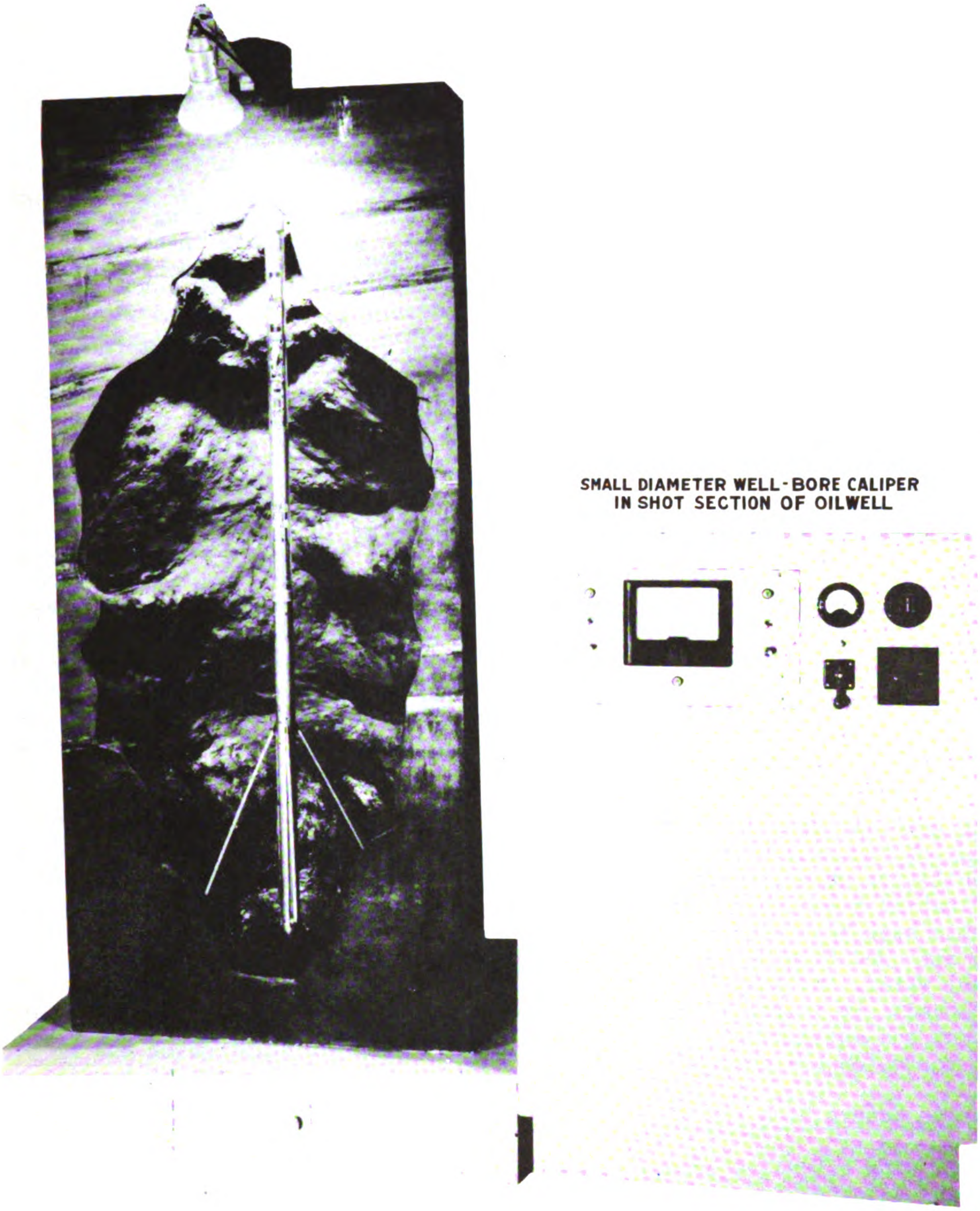

Figure 8. - Small-diameter well-bore caliper as displayed at International Petroleum Exposition.

From the study it was found that each water-injection project presents a different problem in conditioning water. Samples of the water to be used must be obtained and analyzed, and the treating plant must be designed and constructed to meet the specific problems that are involved most efficiently. Characteristics of the available water often are the chief factor in choosing the type of plant (open, closed, or semiclosed) to be used. Samples of the water from the oil-producing formation also should be analyzed. The effects of mixing the brine with the makeup water should be determined, either by a hypothetical combination of the ions present in the two waters or by actually mixing the waters and analyzing the mixed water and any solids precipitated as a result of mixing. An adequate investigation of the characteristics of the waters to be used may eliminate costly errors in plant design.

The design of the conditioning plant and the chemical treating methods used should be, for economic reasons, as simple as is practical to condition the water adequately. Where a closed system is practicable, it is well to use it, as the initial investment cost is less and the operating expense is lower than with an open system. However, closed systems seldom are applicable to waters having high concentrations of suspended matter, dissolved iron, or dissolved acidic gases, especially hydrogen sulfide. Suspended matter necessitates filtration of the water, and filtration is not as simple in a closed system as in an open one. Filters used with closed systems generally are the element type. It is difficult to maintain a completely airtight closed system, and any oxygen introduced into the water may cause oxidation of ferrous iron and its subsequent precipitation as ferric hydroxide. Hydrogen sulfide in appreciable quantities in the water promotes corrosion and is responsible for formation and precipitation of iron sulfide, which has a pronounced plugging action on the face of the oil sand. However, several closed systems apparently are being used successfully in Washington County, Okla., to inject water from the Arbuckle formation containing high concentrations of dissolved free carbon dioxide but no hydrogen sulfide.

In general, corrosion is a more serious problem in the Midcontinent area than plugging of the sand face in water-input wells or voids in the sand. Porosities and permeabilities of oil-bearing rocks usually are high enough to permit the use of water that is reasonably well conditioned. In the few instances observed where input wells have been completely plugged, it usually may be traced to laxity in analyzing and conditioning the water. Corrosion, however, always occurs to some extent with any water, and with some waters it is quite severe unless the water is properly conditioned. It is possible, however, to minimize corrosion, and with the present high cost and scarcity of metal, particularly pipe and tubing, extensive measures to reduce corrosion are economically justified.

Tracers in Waters Used for Subsurface Injection

Following extensive laboratory tests using long sandstone cores, radioactive iodine was selected as a possible tracer for water injected into subsurface strata. Two series of field tests were made in the Bartlesville sand in northeast Oklahoma in which radioactive iodine was added to water injected into the oil sand on a water-flooding project. Iodine 131 has a half life of 8.0 days and a fairly hard (0.64 Mev) gamma radiation, making it suitable for subsurface, as well as surface, detection. It is hoped that through these and similar tests, it may be possible to develop a suitable tracer and techniques to determine the rates and pattern of flow from water-injection wells and the zones of excessive water production in oil-producing wells.

The first series of tests was made to determine if radioactive iodine would pass from a water-injection well to the surrounding producing wells through the pores of the reservoir rock (as indicated affirmatively in laboratory tests) under circumstances in which dyes were completely adsorbed in the formation. Quantities of 1, 25, and 100 millicuries of iodine were used on successive tests. The iodine was detected in some of the offset wells but not in proportion to the quantity injected. Contrary to original information, it was found that one of the wells used in the tests was not properly completed, and it is throught that the erratic appearance of the iodine resulted from the loss of water through that well to improperly plugged and abandoned wells on the edge of the property.

The second test was made where it was known that there was extreme channeling between the input well and the surrounding producing wells. The purpose of this test was to determine if it is possible by using iodine 131 as a tracer of injected water to determine the zones of excessive water production by subsurface detection of radioactivity in the producing wells. Before the tracer was injected, a log of the gamma rays emitted by naturally radioactive material in the formation was made with a subsurface ionization-chamber-type instrument. The instrument was left in a well at a point where excessive water production was expected, and the radioactive iodine was added to the water going to the input well. Approximately 2 hours later the tracer began entering the well containing the logging instrument, as indicated by a substantial increase in radioactivity. Repeated logs made in this hole showed that the tracer was entering through two zones rather than through only one as previously thought. Radioactivity determinations made on the water produced from the well showed that approximately 90 percent of the iodine injected was recovered from this single well. The results of the logging tests as shown in figure 9 demonstrate that under these conditions it is practical to determine zones of excessive water production by using radioactive tracers. The method was demonstrated by an animated exhibit at the International Petroleum Exposition, as is shown in figure 10.

Instruments have been assembled and constructed for continuously monitoring radioactivity background at four producing wells simultaneously in future field tests to be made with radioactive tracers. Repeated radioactivity surveys made during the progress of the laboratory and field tests showed that the work can be done without appreciable exposure to radiation, even when 100 to 250 millicuries of iodine are handled.

Resistivity of Formation Waters in North Texas

A survey was completed and published on the resistivity of subsurface formation waters in the North Texas area.[23] This study was in cooperation with the North Texas Oil and Gas Association and was prepared to increase the reliability of quantitative interpretations with electric logs in the North Texas area. The report covers 14 counties in the North Texas area and presents water-resistivity information from 638 water samples that were collected throughout the area. The resistivity data were obtained by either direct measurement with a resistivity meter or calculated from the chemical analysis of the brine. The locations of the water samples that were collected are shown on maps of each county, and the resistivities of the samples collected from each county are tabulated for convenience. This information is beneficial to oil operators because it determines one of the main unknown factors in applying mathematical equations to the quantitative interpretations of electric logs.

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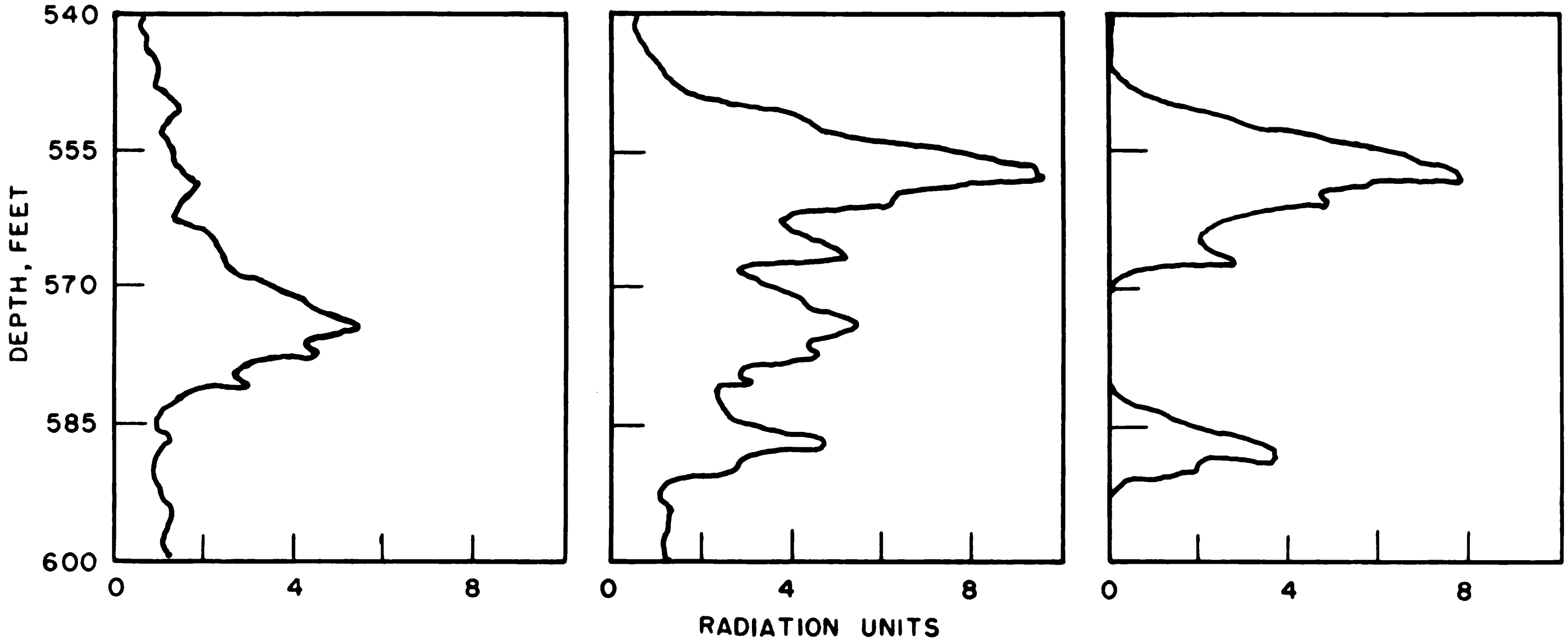
[23] Ayers, M. L., Dobyns, R. P., and Bussell, R. Q., A Survey of Resistivities of Water in Subsurface Formations in North Texas: Petrol. Eng., vol. 24, No. 13, December 1952, pp. B-36-48; also North Texas Oil and Gas Association Cooperative Report 1, December 1952.



A.- NATURAL RADIOACTIVIY OF PRODUCING WELL.

B.- RADIOACTIVITY AS WATER TRACER ENTERS WELL.

C.- (A—B), RADIOACTIVITY INDICATING POINTS OF EXCESSIVE WATER ENTRY INTO WELL.

Figure 9. - Gamma-ray logs obtained in water-productivity logging using radioactive water tracer.

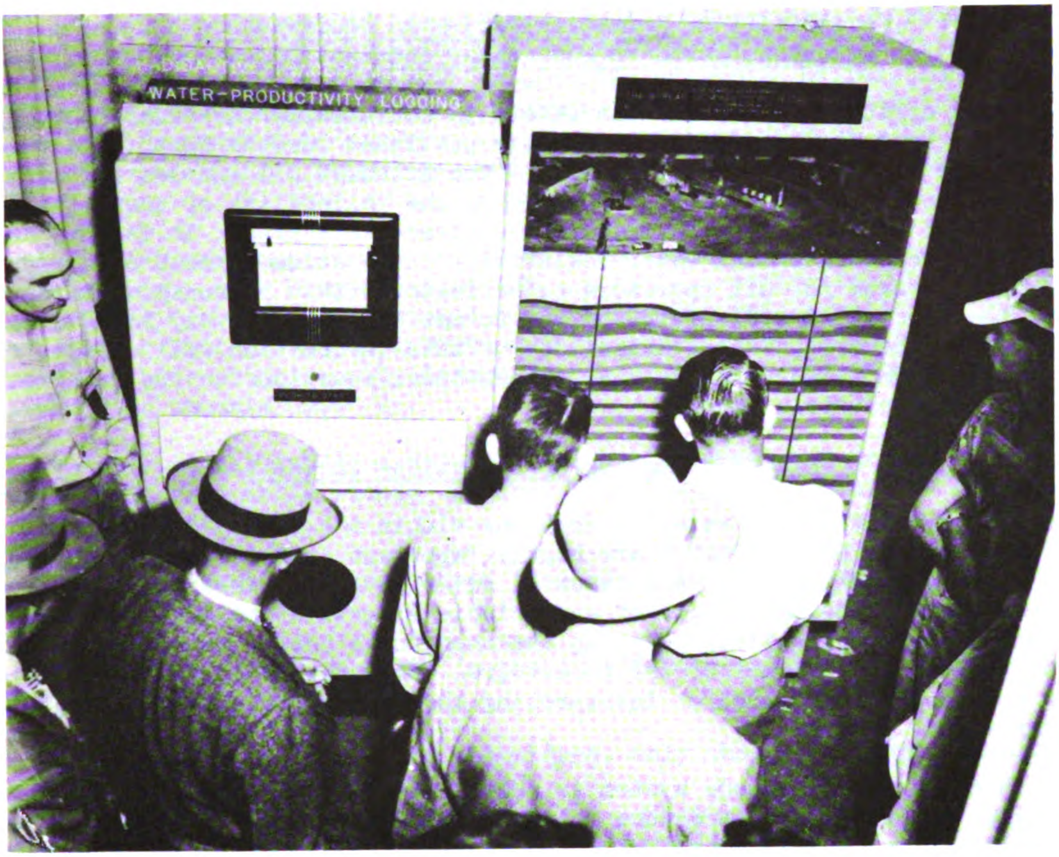


Figure 10. - Exhibit at International Petroleum Exposition demonstrating the use of a radioactive tracer in secondary-recovery operations.

Resistivity of Formation Waters in Southwestern Arkansas, Northern Louisiana, and East Texas

The study of subsurface formation waters in southwestern Arkansas, northern Louisiana, and East Texas, similar to the one published for the North Texas area, was begun. The study is in cooperation with the Arkansas Oil and Gas Commission and will provide information that will increase the reliability of quantitative interpretations of electric logs throughout the three-State area. It is intended that the report will contain enough water-resistivity information on each oil-producing formation in the area for oil operators to estimate, within reasonable limits of accuracy, the electrical resistivity of the formation water for any formation at any location within the area. The availability of this information will eliminate one of the main unknown factors in applying mathematical equations to the quantitative interpretation of electric logs.

Electric Logging of Formations in Wells

Accurate evaluations of water saturations within the partly depleted oil reservoirs of the Eastern United States are highly important in determining the projects in which water flooding will be a successful oil-recovery process in secondary-recovery operations. The usual lack of appreciable structure and edge water and the rather long oil-producing lives point up the need for a better method of determining the present water saturations of the reservoirs. Emphasis of current work is on developing a quantitative method of interpreting shielded monoelectrode logs to obtain this information.

The shielded monoelectrode system is suited to sampling the characteristics of thin sections making up the sandstone column exposed in a well drilled through the oil-producing formation. A method of interpretation was developed in laboratory experiments at Franklin, Pa., and is being tested in the field. Truck-mounted, hydraulic reeling equipment, the electrical circuit, and the depth-measuring device were designed, assembled, tested, and calibrated. Eight wells in the Titusville - Clintonville, Pa., area have been logged electrically, and the interpretations gave water saturations comparable to those obtained in oil-base mud-coring tests in the same areas. A survey of properties of local oil-field brines is being made in connection with these resistivity measurements.

Selective Plugging of Air- and Gas-Injection Wells

Many secondary-recovery, gas-injection projects in the Appalachian area have been in operation for 15 years or more. During this production period, while the reservoir was subjected to gas-injection, the strata possessing the highest permeability to gas were depleted of recoverable oil before the remaining, less permeable strata could be exploited. The movement of gas through the more permeable strata from injection to producing wells without moving a substantial volume of oil is commonly known as bypassing. Plugging of the more permeable, semibarren zones to minimize or eliminate bypassing and permit gas injection into the less permeable, high oil saturated zones is one of the major problems facing operators of air- and gas-injection projects.

The results of laboratory and field experiments conducted to study the effects of plugging oil reservoir sandstones with metallic oxide smokes are being prepared for publication.[24] The smokes investigated in the laboratory for their selective plugging properties were titanium dioxide, stannic oxide, and silicon dioxide, which are readily formed from their respective metallic chlorides by reaction with water vapor in air or gas. Titanium dioxide produced the most dense smoke, and the particles formed and suspended in air were very hard and insoluble in all fluids present in oil-bearing reservoirs; therefore, this plugging medium was selected for field testing.

A field test was completed on an 18-acre portion of Quaker State Oil Refining Corp. Dunham lease, near Pleasantville, Pa. A surface-controlled, bottom-hole, smoke-generating bomb was designed and constructed for use in wells equipped with 2-inch or larger tubing. Three injection wells were treated with titanium dioxide smoke, and the hydrochloric acid, formed as a byproduct of the smoke generation, was neutralized with ammonia gas.

An analysis of all injected and produced gas volumes, and weekly oil- and water-production rates from wells within the area affected by the selective plugging experiment indicated that:

1. Titanium dioxide smoke as used in conjunction with ammonium chloride smoke will plug gas-injection wells.

2. Production data from wells in the immediate area show the plugging was selective.

3. With present equipment and techniques, only chemically pure titanium tetrachloride should be used to generate smoke.

Flowing of Oil Wells on Gas-Injection Projects

The conversion of pumping to flowing oil wells on gas-injection projects was initiated to assist the operators in the Appalachian area to meet their two main objectives: (1) To lower lifting costs, and (2) to improve the efficiency of present air- or gas-injection practices. Production histories of flowing wells were analyzed to determine flow characteristics resulting from flowstring designs based on laboratory experimental data and to evaluate flowing in terms of development and operational costs. The results of a field study on flowing wells in Pennsylvania were published.[25]

The laboratory phase of the flowing problem is being conducted to provide research data necessary to engineer successful field flowing projects. A 10-foot, model air-lift well fabricated from clear plastic tubes is being used for this investigation. Tests were conducted to define the effects of liquid viscosities and flow-string design on flowing efficiencies. No mathematical relationship has been established yet between flow efficiency and viscosity; however, efficiency curves plotted from laboratory data show viscosity to be a significant factor in flowstring design.

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[24] Ball, P. T., Selective Plugging of Gas-Injection Wells With Smoke on a Secondary Oil Recovery Project: Pres. spring meeting, Eastern District Division of Production, API, Pittsburgh, Pa., Apr. 8-10, 1953; Prod. Month., vol. 18, No. 5, March 1954, pp. 24-35.

[25] Grant, B. F., Bossler, R. B., and Rough, R. L., Effect of Flowing on Oil Production From a Secondary Recovery Air-Injection Project in Pennsylvania: Pennsylvania State College, Mineral Industries Experiment Station Bull. 60, 1952, pp. 15-21; also Prod. Month., vol. 17, No. 2, December 1952, pp. 16-21.

Work was discontinued on the flowing-well, gas-injection project in Anderson County, Kans., as the gas-injection operation is to be replaced by water flooding. Because of the haphazard injection of gas and inadequate records, it was not possible to draw any conclusions as to the effect of flowing the wells on the rate of oil production or on the ultimate recovery. No additional flowing projects will be initiated in the Midcontinent area as the injection pressures ordinarily used are too low to make flowing possible and there is little interest in gas injection in this area because of the wide-spread application of water flooding.

Shooting Oil and Gas Wells With Explosives

During the past 60 years shooting has been employed as a routine technique for completing, as well as reconditioning, oil and gas wells in the Appalachian area. Although many investigations based on both the analysis of production rates as measured before and after shooting, and on theoretical conditions, have resulted in improvements in shooting technique, no study has been made that would yield suitable criteria for designing the most efficient explosive charge for any given well. The general objective of the Bureau's research program is to develop the basic fundamentals governing well shooting (by correlating the changes in fluid conductivity of shot holes with the type of explosive, the methods of loading, stemming, and firing, and the physical properties of the rocks) so that more efficient explosive charges can be used with improved techniques to obtain optimum fracturing and minimum crushing of oil-bearing formations.

The 1952 experiments conducted in a shallow sandstone formation were designed to verify and extend the 1950 correlations between strain and pressure measurements recorded in water-filled rock when shot. Additional data were obtained from velocity meters, accelerometers, and seismometers to supplement these measurements. From the consistent and reliable correlation of strain records with pressure measurements, it was concluded that piezoelectric pressure gages suspended in a liquid-filled hole could be used to measure strain. The instrumentation of deep liquid-filled holes is now feasible and can be readily and easily installed by using pressure gages, whereas former procedures of setting, orienting, and cementing strain gages in these holes presented a difficult, if not impossible, task.

The physical properties of typical reservoir rocks are being studied at the Bureau's College Park, Md., Experiment Station. Until recently physical property testing has been confined to dry core samples. A limited number of tests on liquid-saturated samples have indicated that the presence of water or oil in the rock significantly alters some physical property characteristics. An extensive program has been initiated to define variation limits of the physical properties of rock when subjected to different saturations of water and/or oil.

Laboratory Studies

Core and Water Laboratory

Work performed in the core- and water-analysis laboratory at the Bartlesville Station during the year provided basic data for petroleum engineering studies of the Healdton field, Carter County, Okla., and the Flat Rock field, Osage County, Okla., and for a survey of the characteristics of Oklahoma oil-field brines. A survey of the characteristics of Kansas oil-field brines also was completed, and the results were published.26/

26/ Rall, Cleo G., and Wright, Jack, Analyses of Formation Brines in Kansas: Bureau of Mines Rept. of Investigations 4974, 1953, 40 pp.

Water analyses assumed new importance as water flooding was widely adopted in the Midcontinent area as a secondary-recovery practice. The choice of a closed or an open injection system for a water-flooding project, the treatment of injection water, and the compatability of the water to be injected with the connate water of the oil sand are based on the characteristics of the available water, as indicated by laboratory analyses. The development of electric-logging devices and the increasing interest in the interpretation of these logs have further augmented the need for analyses of formation brines. The report on Kansas oil-field brines includes the mineral analysis of 600 samples and the measurement of the resistivity of each sample at several temperatures. These data should meet a long-standing need for such records.

Statistically the work of the laboratory included complete mineral analyses and resistivity determinations on 158 samples and partial analyses on 330 samples. Core analyses made during the year included 80 flood-pot tests, 275 porosity measurements, 204 permeability measurements, 150 liquid-saturation measurements, and 290 determinations of connate water content.

An accurate and rapid method of determining the bulk volume of core samples for porosity determinations with the commonly used (electrical contact) bulk volume cell was described by Hamontre and Rall.[27] This apparently simple device was carefully studied, and a unit believed to be superior to those used previously was developed. The new unit does not differ greatly from those used before, except that an electronic circuit is used to eliminate arcing between the micrometer tip and the mercury. Other differences consist principally of more precise workmanship. Errors have been reduced to less than 1 percent, but the cell developed does not give the accuracy that may be obtained by the careful use of a pycnometer, although it is satisfactory for most routine work.

The laboratory core-testing facilities at the Franklin office were expanded during 1952-53. Equipment required to determine minimum interstitial water contents of small core samples by both the evaporation and capillary desaturation methods were placed in operation. A refrigerated, high-speed centrifuge now being fabricated will be used as a third method for minimum interstitial water content measurements. Other special equipment now being constructed includes a recently designed bulk volume measurement apparatus, glass capillary desaturation cells, Hassler-type core holders, and a porosity cell for the gas-expansion type porosimeter.

Restored state (capillary desaturation) tests were continued on core samples from producing formations in the Appalachian region that were acquired during the oil-base and mud cable-tool coring program. The technique of capillary desaturation is that of displacing water from an originally water-filled sample by applying pressure to the displacing phase, generally air or nitrogen, and occasionally oil. Water-content data from both the restored-state method and routine core analysis are being compiled for evaluation.

An investigation of the capillary desaturation versus the evaporation method was begun to compare the relative merits and results of the two techniques. The evaporation method involves the continuous weighing of a core sample originally saturated with water. During the weighing process the water in the sample is evaporated by a continuous stream of air directed over the core. Continuous automatic weighing provides a means of calculating the rate of evaporation. The values of interstitial water determined by this method on a limited number of samples were within 5 percent of those obtained by capillary desaturation.

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[27] Hamontre, H. C., and Rall, Cleo G., Improved Bulk-Volume Cell Speeds Porosity Determinations: Oil Gas Jour., vol. 51, No. 37, Jan. 19, 1953, pp. 94-6.

At the Laramie station the laboratory study of the physical characteristics of oil reservoirs having secondary-recovery possibilities was restricted to an investigation of the Newcastle sandstone in the Fiddler Creek, Wyo., area and the Frontier formation in the Big Horn Basin, Wyo. Cores representing 830 feet of producing formation from 22 wells in the 15 fields were analyzed. These analyses included the following numbers of determinations: 582 air permeabilities, 394 liquid permeabilities, 724 porosities, 113 oil and water saturations on fresh cores, 159 clay separations, 61 clay identifications, and 90 series of oil-recovery tests on radial samples.

Analysis of the results obtained on samples of the Newcastle sandstone reservoir at Fiddler Creek, Wyo., led to the following conclusions: (1) Salt water could be successfully injected into the reservoir for secondary recovery, (2) most of the material of clay size in the rock is not a clay mineral but is fine silica powder, (3) the predominant clay mineral present is not bentonite, as previously assumed, but is kaolin, and (4) water is a more efficient driving medium to displace the oil in the reservoir of the producing well than is gas. A report for publication containing these conclusions and other important information is being prepared.

Study of Pore Size, Shape, and Pattern of Sandstones

Some of the more active phases of the study of reservoir rock characteristics are studies of clay minerals in the rocks, the effect of waters on the rocks, and possible remedial treatment for water-blocked oil formations. Preliminary clay mineral identification tests by staining techniques have been made on 52 samples of 17 oil-producing formations from 30 fields of Pennsylvania, West Virginia, Ohio, and Kentucky. Reactions for identifying montmorillonite (swelling-type clay mineral) were strong for 10 samples, moderately strong for 3 more samples, and weak or none for the remaining samples. The 13 samples showing the stronger reactions were of the same producing sandstone from 5 oil fields. Samples of the same formation from four other fields gave weak or no reaction. Equipment for more quantitative analyses by differential thermal and X-ray techniques as well as fluid-flow tests on sandstone specimens is being assembled. This work is directly related to the problems of increasing the efficiency of petroleum-production methods. The choice and treatment of flooding waters are most important in connection with rocks that contain clay minerals that are dispersed by some water.

Equipment is being assembled for determining relationships between equivalent pore-entry radii and the pore volume associated with each value of pore-entry radius by the mercury injection technique. Equipment is also being assembled for relative permeability determinations to be used in evaluating the oil-recovery characteristics of petroleum reservoir rocks.

The program of secondary-recovery research in California includes a group of experiments designed to evaluate the fundamental properties of California reservoir rocks that influence the efficiency of oil recovery by water flooding, including surface areas, pore geometry, wettability, and relative permeability to oil, gas, and water (two-phase flow only).

Surface Areas of California Cores

Experimental work has been completed on the problem of measuring surface areas of sands and clays, and the results will be published in a technical journal.

Surface areas of several California sands and clays were determined quantitatively by adsorption of stearic acid from benzene and methanol solution on the exposed surface areas.

The amount of stearic acid adsorbed from the benzene solution was obtained gravimetrically after the solvent evaporated and from the methanol solution by titration with standard alkali, using electrical conductivity to determine precisely the end point of titration. Throughout the investigation a critical comparison was made of the gravimetric and volumetric methods with respect to (1) accuracy, (2) speed, (3) adaptibility to the particular problems of measuring the surface areas of oil-producing sands. One of the important experimental procedures noted was that electrical conductance rather than resistivity of the solution should be utilized to determine the endpoint of titration precisely, as the straight lines obtained can be interpreted much more accurately than the curved plots obtained with resistivities. An additional improvement in experimental procedures was determination of the optimum concentrations of stearic acid in both the benzene and methanol solutions and of the optimum amount of water to add to the latter solution for ease of measurement by electrical conductance.

Pore Geometry of California Cores

The tortuosity of pores within a rock is the ratio of the tortuous length of the pore channels between two parallel surfaces of the rock to the distance between the surfaces. It is determined as a function of the transit time of chloride ion through the pore channels as compared to that through straight capillaries. The rock sample must be freed of chloride salts and saturated with a chloride-free electrolyte before measuring the tortuosity. When the tortuosity of enough California oil sands has been determined, an attempt will be made to determine a relation between tortuosity and the recovery of oil from the sands.

An apparatus for measuring tortuosity was fabricated and assembled, and design modifications were incorporated to stabilize operation. The tortuosity factor of a sample of San Jose sandstone was determined under various conditions of potential gradient and current flow to establish the reproducibility of the method. A means of purifying the core sample by electrodialysis before testing was devised.

Recovery Efficiency of Water-Flooding High-Viscosity Oils

In the San Francisco laboratory a second series of water-flooding experiments to determine the effect of oil viscosity on recovery was completed. The viscosities of the oils used in these experiments ranged from 1 to 950 centipoises. A study of anomalous results obtained from these series of floods brought to light the possibility that the varying interfacial tension between the brine and the various oils used had a greater influence upon oil recovery than was generally believed heretofore. Supplementary experiments were conducted in which the interfacial tensions were controlled. Preliminary treatment of the data obtained indicates that the anomalies encountered in the previous experiments were caused by variation in liquid-liquid interfacial tension - particularly in the range of lower oil viscosities. Previous investigators have given some attention to the qualitative effect of this variable, but little experimental work has been done to evaluate quantitatively its influence upon the amount of oil recoverable by water drives. Accordingly a quantitative evaluation of the effect of interfacial tension will be attempted in treating the data obtained in this project.

Gravity Drainage of Oil From Unconsolidated Sands

The results of laboratory studies of the factors affecting the recovery of oil by gravity drainage from unconsolidated sands were reported.[28] Experiments described in this report supplement earlier laboratory drainage tests in which data were obtained on gravitational drainage of heavy oil from unconsolidated sands and on the effect of heat upon additional oil recovery after no more oil drained from the sand under the influence of gravity.[29] After the tests were completed, the sand was cored, and segments of the cores from around the immediate vicinity of the tunnel were found to be caked with altered oil. As a result, a series of followup experiments, using sand-packed columns, was conducted to ascertain the extent of caking and its influence on the drainage of oil and to obtain additional information regarding the effect of heat on gravity drainage. Data also were obtained on the effect of such factors as the viscosity of the oil, interstitial water, grain size, and sand thickness on the gravity drainage of oil from sand-packed columns.

The results showed that drainage decreases as the viscosity of the oil increases and as the quantity of the interstitial water increases; that the larger the sand grains and the thicker the formation the greater the recovery. For the application of heat to aid in the recovery of low API-gravity oils, the sand body must be heated throughout and the oil saturation must be high. The recovery of light-gravity crude oils was not increased appreciably by using heat because the drainage by gravity was so thorough that the remaining oil was not freed by heat. The report presents reservoir and production data on 10 fields where gravity drainage will or has resulted in high recovery of oil. Data are presented that show in some fields recovery by gravity drainage will exceed that which would be obtained by water-flooding.

Reservoir performance data from fields in the United States and South America were studied to ascertain if the factors that influence gravity drainage in the laboratory also will influence drainage in a comparable manner in the reservoir. The results of the analysis of the field data and some of the pertinent information pertaining to the reservoirs are presented in a section of the report.

Corrosion of Metals by Dissolved Gases in Water

Corrosion of metallic equipment is a serious economic problem in the production of petroleum and, particularly, in the secondary recovery of petroleum by water flooding. Despite the tremendous amount of fundamental and applied research performed on corrosion problems, few data are available concerning the corrosivity of dissolved oxygen, free carbon dioxide, and hydrogen sulfide in the concentrations and ratios and at the temperatures usually encountered under actual oil-field conditions. The tests began in 1952 to determine the corrosion caused to a mild steel in water by dissolved gases were continued, and a progress report[30] was presented at the 123d annual meeting of the American Chemical Society.

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[28] Higgins, R. V., Factors That Influence Gravity Drainage: Petrol. Eng., vol. 25, No. 5, May 1953, pp. B-83 - B-93.

[29] Higgins, R. V., and Shea, G. B., Laboratory Studies of the Gravitational Drainage of Oil from Unconsolidated Sands, Bureau of Mines Rept. of Investigations 4391, January 1949, 15 pp.

[30] Watkins, J. W., and Wright, Jack. Corrosive Action of Dissolved Gases on Steel in Water: Pres. 123d Ann. Meet. Am. Chem. Soc., Los Angeles, Calif., Mar. 16, 1953.

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The data obtained on the corrosion of dissolved oxygen, hydrogen sulfide, and carbon dioxide are shown graphically in figure 11. These data were obtained with the variables of temperature and velocity maintained constant and with other factors influencing the rate of corrosion, such as galvanic action, eliminated insofar as possible. Consequently, the use of these data in precisely predicting corrosion should be limited to similar conditions. However, it is believed that they may be used as criteria with reasonable accuracy if it is recognized that much corrosion may be caused by other factors.

The laboratory tests are being continued using different ratios of oxygen to free carbon dioxide as corroding mediums. Data obtained in this study should be useful to oil producers in general and secondary-recovery operators in particular in predicting the potential corrosiveness of waters produced with petroleum and used for injection in secondary-recovery operations.

Retention of Petroleum by Reservoir Rocks

Fluid-Flow Phenomena

The nature of fluid flow through a porous solid medium has long been the subject of investigation and speculation, but the problem has not been satisfactorily solved. One particular difficulty is that the role of special forces, often referred to as surface forces at the solid-liquid interface, is not completely understood. Precision permeability measurements of several quartz-powder beds were made in which small but reproducible differences in the permeability of a given plug to different pure liquids and solutions were observed. For stable inert systems permeability may be described by the Kozeny-Carman equation when the porosity of a packed bed is uniform enough to result in liquid flow over the entire particle. Such conditions were attained when the powder was dispersed by the liquid.31/

The same methods and instruments developed in earlier permeability studies are being used to study the effect of wettability and other surface forces on the permeability of Alundum (aluminum oxide) plugs sealed in pyrex. The stability and chemical inertness of the Alundum plugs allows the observation of differences in permeability so small as to go unnoticed in less stable systems.

A standard gas-adsorption apparatus (fig. 12) has been constructed to measure surface areas and constants of the Alundum plugs and powders studied so as to provide a basis for the analysis of surface forces.

Further advances have been made in theoretical and experimental studies of the effects of electrical and electrokinetic (changes in motion produced by electrical forces) phenomena on the flow of fluids through porous mediums. It is known that the tendency of petroleum to cling to the walls of the rock pores in which it occurs, rather than to flow freely through those pores as forced by pressure in the reservoir, is caused by a number of physical factors. Among those factors are certain electrical and electrokinetic phenomena. Information on the fundamental principles of those forces and their phenomena is essential to an understanding of their significance in the production of petroleum by applying pressure from external sources (secondary-recovery methods) and to understanding means of promoting more complete recovery of petroleum by utilizing the beneficial electrokinetic effects and minimizing the undesirable ones. The pressure-decline technique previously developed to measure permeability has been extended to measurements of streaming potential, streaming current, and electroosmotic pressure. For the first time,

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31/ Johansen, R. T., Lorenz, P. B., Dodd, C. G., Pidgeon, F. D., and Davis, J. W.: The Permeation of Water and Iso-octane Through Plugs of Microscopic Particles of Crushed Quartz: Jour. Phys. Chem., vol. 57, No. 1, January 1953, pp.40-45.

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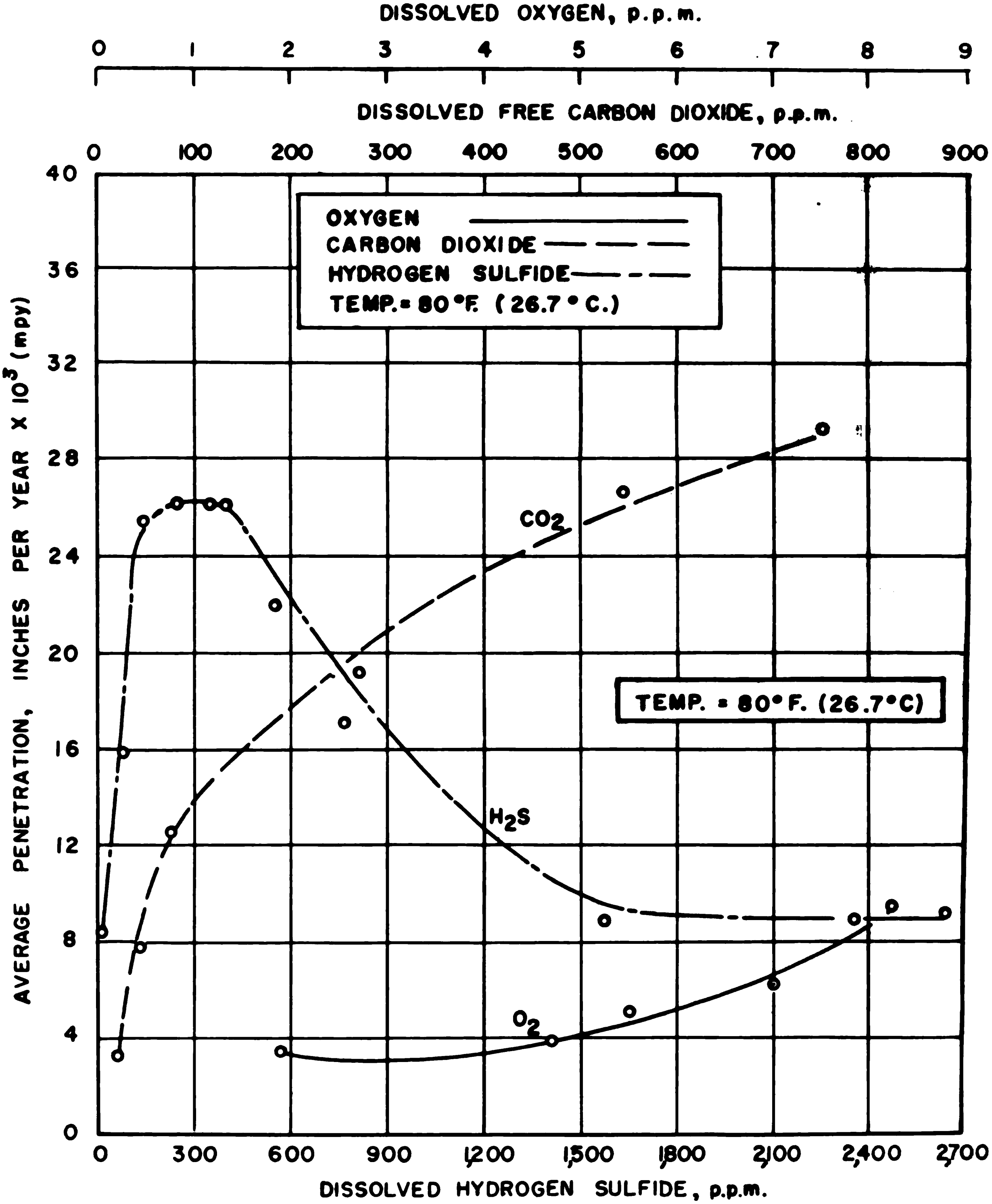

Figure 11. - Comparative corrosive action of oxygen, free carbon dioxide, and hydrogen sulfide on steel in distilled water.

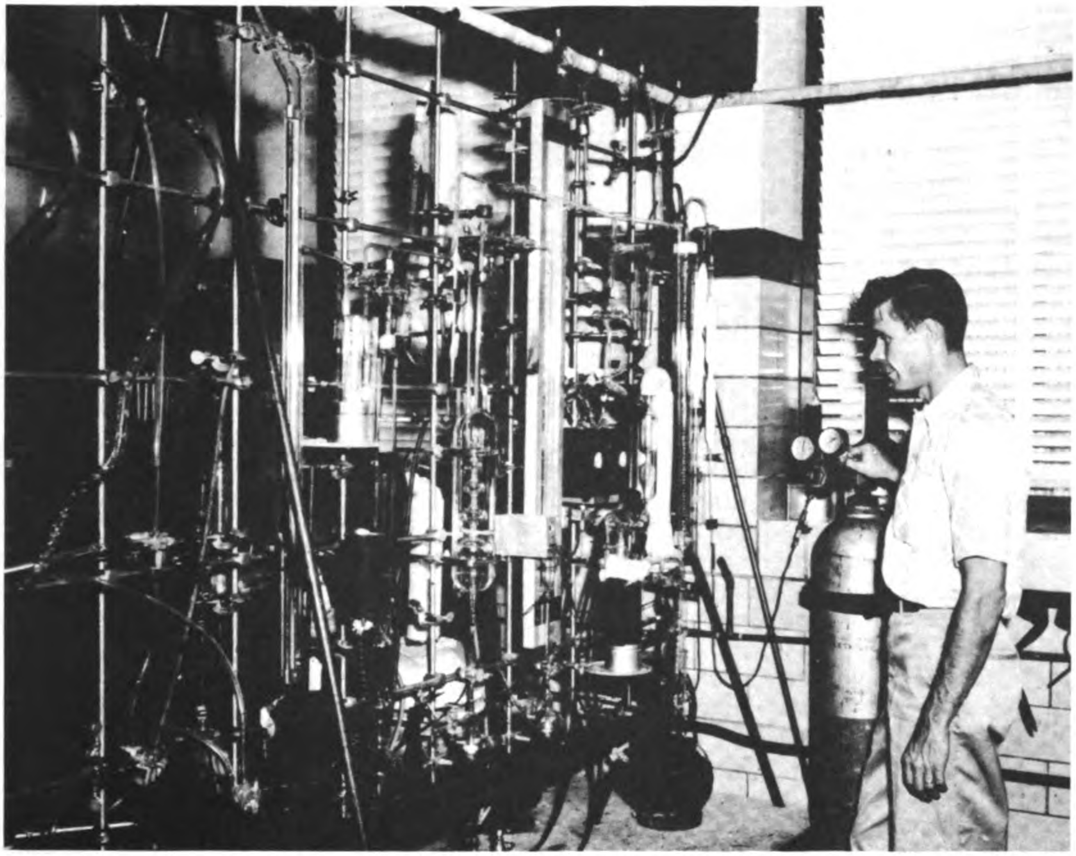

Figure 12. - Gas adsorption apparatus for measuring surface areas.

with a nonaqueous liquid, Saxen's law relating streaming potential and electroosmosis has been verified.[32] Also for the first time, the electroviscous and electroosmotic conductance effects were measured directly and found to be 0.9 percent, in fair agreement with theory.

It has been established that when two porous mediums exhibiting electrokinetic effects are combined in parallel or series, the ordinary laws of combination of electrical resistance are slightly altered. The exact laws have been derived[33] by a general treatment, which also gives combination laws of permeability, streaming effects, and electroosmotic effects.

Detergency in Petroleum Production

The program for evaluating detergents as additives in water-flooding operations was continued. Over 100 different detergents have been rated for their efficiency in displacing crude petroleum from sand by a centrifugal method. The displacement efficiencies of these detergents can be correlated with other properties such as solubility, cloud point, wetting action, surface activity, and emulsifying capacity. The results of these tests give conclusive evidence that such additives can increase the centrifugal displacement of crude petroleum from unconsolidated sand. Other tests, including flooding packed sand columns and synthetic and natural cores, have been carried out to establish the relationship of the laboratory centrifugal tests to field operations.

The fundamental phases of the study of detergency in petroleum production have received careful attention. A series of detergents, labeled with radioactive carbon, has been obtained, a comprehensive study of tracer instrumentation and technique has been made, and the adsorption isotherm of a nonionic detergent on sand has been determined by tracer methods. This is one of the first adsorption isotherms of a nonionic detergent ever to be determined by radioactive tracer methods and thus represents a significant advance in scientific methods.

Reservoir Materials

Preliminary studies of the effect of detergents upon the swelling and flocculation of clays have been initiated. Though field tests of the lowering of residual oil in a reservoir by the use of surface-active additives have been rather inconclusive, it has been established that under proper conditions detergents may be used to increase the permeability of a formation to water.

A color test[34] based on the adsorption and oxidation of p-amino phenol on clay mineral surfaces has been developed for routine identification of the principal clay mineral groups, the montmorillonoid, illite or hydrous mica, and kaolin families. The new test has been found to compare favorably with other staining and color tests currently in use. The procedure involves the use of alcoholic solutions of p-amino phenol of varying concentrations, followed by treatment with hydrochloric acid. Tests are carried out on white porcelain spot plates and colors are observed both wet and dry, using reflected light and standard color chips of the Munsell color system.

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[32] Lorenz, P. B., Electrokinetic Relations in the Quartz-Acetone System: Jour. Phys. Chem., vol. 57, No. 4, April 1953, pp. 430-4.

[33] Lorenz, P. B., Electrokinetic Processes in Parallel and Series Combinations: Jour. Phys. Chem., vol. 57, No. 3, March 1953, pp. 341-3.

[34] Hambleton, W. W., and Dodd, C. G., A Qualitative Color Test for Rapid Identification of Clay Mineral Groups: Econ. Geol., vol. 48, No. 2, March-April 1953, pp. 139-146.

The test has been found to be most sensitive and accurate for members of the montmorillonoid family. Its application to identification of illites or hydrous micas is only slightly less satisfactory. Kaolin minerals are identified with ease, except in mixtures where these minerals are minority constituents.

Surface-Active and Film-Forming Constituents of Petroleum

A knowledge of the identities and properties of petroleum constituents having a high degree of interfacial activity is a requisite to understanding the forces that may affect or control the success of secondary-recovery operations, breaking of stable oil-field emulsions, and removal of certain trace metals from petroleum before treatment with expensive and easily poisoned catalysts.

A California crude oil has been fractionated[35] by solvent extraction supplemented by chromatographic procedures. The interfacial activities, film-forming tendencies, concentrations of metal-porphyrin complexes (derivatives of chlorophyll and hematin), and free porphyrin concentrations for the various extracts have been determined. The metal-porphyrin complexes have been degraded and then resynthesized.

The interfacial tension studies corroborate the prevalent assumption that the interfacial activity of a crude oil is associated primarily with its asphaltic content. The results of the study conclusively show the presence of a considerable amount of the nickel-porphyrin complex and indicate smaller amounts of the vanadium-porphyrin complex in this crude oil. Correlations of interfacial activities and porphyrin contents show that the metal porphyrin complexes identified are major contributors to the interfacial activity exhibited by this crude oil. The presence of porphyrins and their metal complexes in petroleum is indicative of the biological origin of petroleum. The stability of the porphyrin complexes of nickel and vanadium may account for some of the difficulties encountered in attempts to remove these metals from crude petroleum.

The pendent-drop method was used to study[36] the interfacial aging of solutions of mesoporphyrin IX, its dimethyl ester, and the vanadium complex of the dimethyl ester. The dimethyl ester in benzene or chloroform exhibited moderate interfacial activity at the water interface. The free acid and the vanadium complex in benzene solutions were considerably more active than the ester. Mesoporphyrin IX and the vanadium complex formed complete solid films after short aging periods at the benzene-water interface. Mesoporphyrin IX dimethyl ester formed no solid film at the water-chloroform interface, and little solid film upon extended aging at the benzene-water interface.

PETROLEUM CHEMISTRY AND REFINING

Research on the chemistry and refining of petroleum was continued with the objective of developing improved relationships between composition of petroleum and utilization of petroleum products. During this year, research on sulfur compounds in petroleum was continued at a high level, and additional emphasis was directed toward relationships between composition of distillate fuels and their stability in storage. Different parts of the program are closely integrated and the same personnel work on different phases of the program, but for convenience it can be discussed under the following headings:

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[35] Dunning, H. N., Moore, J. W., and Denekas, M. O., The Interfacial Activities and Porphyrin Contents of Petroleum Extracts: Pres. 8th Southwest Regional Meeting, Am. Chem. Soc., Little Rock, Ark., Dec. 4, 1952.

[36] Dunning, H. N. The Interfacial Activity of Mesoporphyrin IX and Some Derivatives: Jour. of Coll. Sci., vol. 8, No. 3, June 1953, pp. 279-287; also pres. 122d meeting, Am. Chem. Soc., Atlantic City, N. J., Sept. 16, 1952.

1. Characteristics and Availability of Crude Oil and Products.
2. Sulfur Compounds in Petroleum.
3. Nitrogen Compounds in Distillate Fuels.
4. Chemical Studies of Fuels.
5. Combustion Research on Fuels.
6. Composition and Properties of Asphalt.
7. Fuel Surveys.

Characteristics and Availability of Crude Oils and Products

During the year 209 crude oil samples from domestic fields and 4 samples from 4 foreign fields were analyzed by the Bureau of Mines routine method. Geographical distribution of the samples was as follows:

> Alaska 1, Arkansas 5, California 18, Colorado 6, Canada 2, France 1, Illinois 1, Kansas 1, Louisiana 22, Yugoslavia 1, Montana 12, North Dakota 10, Oklahoma 3, Pennsylvania 1, Texas 71, Wyoming 58.

Many thousands of crude oils have been analyzed by the Bureau of Mines routine method during its more than 30 years of existence. The magnitude of this catalog of crude-oil characteristics enhances the value of each analysis because of the comparisons that can be made. The analyses of 37 crude oils were presented in a report[37] discussing the properties of oils produced in the Powder River Basin of Wyoming. Twenty-one oils from the Williston Basin of North Dakota and Montana have been analyzed, and a report is in preparation. Another report covering the crude oils of Colorado is being prepared. It will include analyses of 63 oils produced from fields in that State.

Several other reports concerning crude-oil analyses are also in preparation. Included among these is an additional tabulation of California.[38] This report will give 88 analyses of crude oils from California analyzed during previous years from Fresno, Kings, Monterey, San Luis Obispo, Kern, Santa Barbara, Ventura, and Los Angeles Counties.

The eighth article of a series regarding refining properties of new crude oils was accepted for publication by Petroleum Processing.[39] The report discusses the analyses of 10 crude oils from the Spraberry, Tex., area and includes octane number and cetane number data on distillates from 2 of the crude oils.

Progress was made toward developing an amplified standard crude-oil analysis method that will provide fractions large enough to determine properties such as octane number and cetane number. Two stills were constructed, each having a maximum charge capacity of 10 liters. One column is 20 inches in height and the other 32 inches, and both are 2 inches in diameter with Stedman screen-type packing. This type packing permits relatively high through-put and fractionating efficiency is relatively unimpaired by water, which is present in many crude-oil samples. Only selected crude oils representative of large production will be analyzed by this amplified procedure, but correlations will be developed to relate these analyses to those made using the standard routine method.

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[37] Wenger, W. J., and Lanum, W. J., Characteristics of Crude Oils From the Powder River Basin: Petrol. Eng., vol. 24, No. 10, September 1952, pp. A60-A71.

[38] Garton, E. L., and McKinney, C. M., Analyses of Crude Petroleum From Some Fields of California: Bureau of Mines Rept. of Investigations. (In press.)

[39] McKinney, C. M., and Smith, H. M., Refining Properties of New Crudes. Part 8 - Crude Oil from the Spraberry, Tex., Area: Petrol. Proc., vol. 8, No. 8, August 1953, pp. 1164-1167.

Sulfur Compounds in Petroleum

The research in this field, known as American Petroleum Institute Research Project 48A, enters its sixth year in August 1953. During the 5 years since its inauguration, outstanding progress has been made in each of the 3 areas of research:

1. Synthesis, purification, and determination of properties of compounds.
2. Separation, isolation, and identification of sulfur compounds in petroleum.
3. Determination of thermodynamic data of sulfur compounds.

The first two phases of this project are conducted at Laramie, Wyo., and Bartlesville, Okla., respectively, and are described below. The third phase is also conducted at Bartlesville and is discussed under the section on Thermodynamics of Petroleum in this report.

Synthesis, Purification, and Determination of Properties of Sulfur Compounds

The research under API Project 48 on the synthesis, properties, and identification of sulfur compounds in petroleum has been described in a recent publication.40/ When the project started, comparatively few data on the physical and spectral properties of sulfur compounds were available. As a result of the project, 24 highly purified (99.9 mol percent or better) sulfur compounds have been prepared. Careful measurements of the properties of the first 20 of these compounds have resulted in obtaining 631 values. The physical properties measured include freezing point, cryoscopic constant, boiling point, viscosity at 3 temperatures, surface tension at 3 temperatures, density at 3 temperatures, and refractive indices for 7 wavelengths and 3 temperatures. Mass, ultraviolet, infrared, and Raman spectra have been obtained so that now 94 spectra are available on compounds of high purity.

In order to utilize smaller samples and to amass data more rapidly - even though it might be of lesser precision - the "small sample" program was started. As a result of this program, some 96 values of physical properties have been added to the literature and 179 spectra have been made available.

The relationship of these two programs is shown in figure 13, as are the steps in the production of the compounds and the measurement of their properties. Also, some of the ultimate uses of the compounds and data are shown. Although the primary uses are within API Project 48, gifts of sulfur compounds are also made available to qualified investigators as an encouragement to research on sulfur chemistry.

During the past year 4 compounds have been added to the list of purified compounds, bring the total to 24. These compounds are listed in table 2 together with their structures and purities. Twenty-four additional compounds have been selected for purification, and they are in various stages of purification.

40/ Ball, J. S., Bordwell, F. G., Smith, H. M., Waddington, G., and Seyfried, W. D.: Synthesis, Properties, and Identification of Sulfur Compounds in Petroleum: Proc. API, vol. 32, sec. 3, 1952, pp. 139-175.

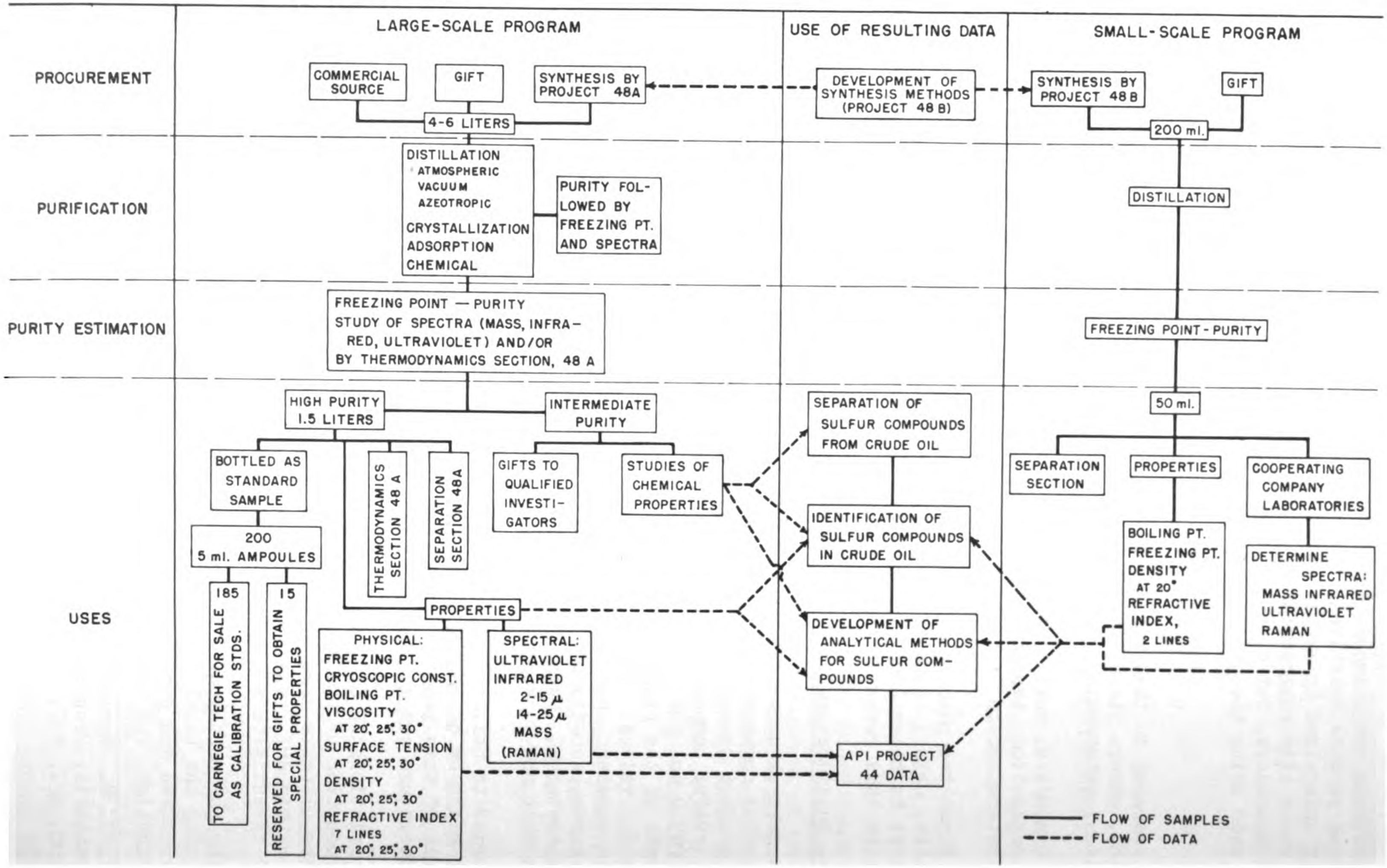
LARGE-SCALE PROGRAM
USE OF RESULTING DATA
SMALL-SCALE PROGRAM
PROCUREMENT
PURIFICATION
PURITY ESTIMATION
USES
COMMERCIAL SOURCE
GIFT
SYNTHESIS BY PROJECT 48A
4-6 LITERS
DEVELOPMENT OF SYNTHESIS METHODS (PROJECT 48 B)
SYNTHESIS BY PROJECT 48 B
GIFT
200 ml.
DISTILLATION ATMOSPHERIC VACUUM AZEOTROPIC CRYSTALLIZATION ADSORPTION CHEMICAL
PURITY FOLLOWED BY FREEZING PT. AND SPECTRA
DISTILLATION
FREEZING POINT — PURITY STUDY OF SPECTRA (MASS, INFRARED, ULTRAVIOLET) AND/OR BY THERMODYNAMICS SECTION, 48 A
FREEZING POINT - PURITY
HIGH PURITY 1.5 LITERS
INTERMEDIATE PURITY
BOTTLED AS STANDARD SAMPLE
200 5 ml. AMPOULES
185 TO CARNEGIE TECH FOR SALE AS CALIBRATION STDS.
15 RESERVED FOR GIFTS TO OBTAIN SPECIAL PROPERTIES
THERMODYNAMICS SECTION 48 A
SEPARATION SECTION 48A
GIFTS TO QUALIFIED INVESTIGATORS
STUDIES OF CHEMICAL PROPERTIES
PROPERTIES
PHYSICAL: FREEZING PT. CRYOSCOPIC CONST. BOILING PT. VISCOSITY AT 20°, 25°, 30° SURFACE TENSION AT 20°, 25°, 30° DENSITY AT 20°, 25°, 30° REFRACTIVE INDEX 7 LINES AT 20°, 25°, 30°
SPECTRAL: ULTRAVIOLET INFRARED 2-15 μ 14-25 μ MASS (RAMAN)
SEPARATION OF SULFUR COMPOUNDS FROM CRUDE OIL
IDENTIFICATION OF SULFUR COMPOUNDS IN CRUDE OIL
DEVELOPMENT OF ANALYTICAL METHODS FOR SULFUR COMPOUNDS
API PROJECT 44 DATA
50 ml.
SEPARATION SECTION
PROPERTIES
COOPERATING COMPANY LABORATORIES
BOILING PT. FREEZING PT. DENSITY AT 20° REFRACTIVE INDEX, 2 LINES
DETERMINE SPECTRA: MASS INFRARED ULTRAVIOLET RAMAN
FLOW OF SAMPLES
FLOW OF DATA

Figure 13. - Preparation and uses of purified sulfur compounds.

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TABLE 2. - Highly purified sulfur compounds

Compound	Structure	Impurity, percent
Thiols:		
Ethanethiol (ethyl mercaptan)	C-C-SH	0.05 ± 0.04
1-Propanethiol (n-propyl mercaptan)	C-C-C-SH	.07 ± .07
2-Propanethiol (isopropyl mercaptan)	C-C-SH C	.02 ± .02
1-Butanethiol (n-butyl mercaptan)	C-C-C-C-SH	.04 ± .04
2-Buthanethiol (sec-butyl mercaptan)	C-C-C-C SH	.1 ± .1
2-Methyl-1-propanethiol (isobutyl mercaptan)	C C-C-C-SH	.01 ± .01
2-Methyl-2-propanethiol (t-butyl mercaptan)	C C-C-SH C	.08 ± .04
1-Pentanethiol (n-pentyl mercaptan)	C-C-C-C-C-SH	.08 ± .05
Benzenethiol (thiophenol)	C-C C C-SH C-C	.02 ± .02
Sulfides:		
2-Thiapropane (dimethyl sulfide)	C-S-C	.01 ± .01
2-Thiabutane (methyl ethyl sulfide)	C-S-C-C	.04 ± .04
2-Thiapentane (methyl n-propyl sulfide)	C-S-C-C-C	.03 ± .03
3-Thiapentane (diethyl sulfide)	C-C-S-C-C	.06 ± .04
3-Methyl-2-thiabutane (methyl isopropyl sulfide)	C C-S-C C	.01 ± .01
4-Thiaheptane (di-n-propyl sulfide)	C-C-C-S-C-C-C	.04 ± .01
Cyclic sulfides:		
Thiacyclobutane (trimethylene sulfide)	S C-C-C	.05 ± .05
Thiacyclopentane (tetrahydrothiophene)	C-C S C-C	.05 ± .05
Thiacyclohexane (pentamethylene sulfide)	C-C C S C-C	.06 ± .06
Disulfides:		
2,3-Dithiabutane (dimethyl disulfide)	C-S-S-C	.03 ± .02
3,4-Dithiahexane (diethyl disulfide)	C-C-S-S-C-C	.10 ± .08
Thiophenes:		
Thiophene	S C C C - C	.013 ± .011
2-Methylthiophene	S C C-C C - C	.04 ± .04
3-Methylthiophene	S C C C - C-C	.03 ± .03
2,3-Benzothiophene (thianaphthene)	C S C C C C C - C C	.032 ± .01

Except for the four compounds completed during the year, property and spectral determinations have been made on all of the compounds. A paper describing the properties of the first 10 compounds prepared was presented.[41]

The effect of the sulfur content of petroleum distillates depends considerably on the type of compound present. Consequently, one of the aims of Project 48 is development of a systematic scheme of analysis for the various types of sulfur compounds present in petroleum. The information developed on the properties of individual compounds is useful for this purpose, but even more valuable is the opportunity to try various procedures on a large number of individual sulfur compounds.

At present one of the recognized methods for sulfur group analysis in petroleum fractions is the analytical procedure developed at the Bureau of Mines in 1941.[42] In testing the effect of the classification reagents used in this method, it was found that, contrary to expectations, several of the compounds usually considered as Sulfides II were removed in significant amounts by treatment with mercurous nitrate. A possible reason might lie in the contamination of the mercurous nitrate by mercuric nitrate, and analyses were made by a semiquantitative method[43] modified to give quantitative results by using a spectrophotometer. However, the difficulty was not entirely caused by presence of mercuric salt, and the dryness of the salt is thought to be a more important factor.

One of the least satisfactory parts of the Bureau of Mines group sulfur analysis is the failure of the method to differentiate thiophene and its homologs from aromatic sulfides. Both types are grouped together as Sulfides II. Although thiophene and its homologs have not been thought to be present in straight-run fractions, more evidence is accumulating to suggest that they might be found. Considerable effort has therefore been expended to develop, from a published procedure, a method suitable for determining the quantity of sulfur present as thiophene and its homologs.

One of the problems started during the residence of a Point IV trainee has been completed and published in the country of origin.[44] Using data on boiling points of sulfur compounds, a relationship with the number of carbon atoms in the molecule was worked out for several homologous series.

Separation and Identification

During the year work was concentrated on identification of sulfur compounds in Wasson crude oil in the 110°-150° C. boiling range. As mentioned in an earlier report,[45] this boiling range distillate was removed from Wasson crude oil and passed through activated alumina to concentrate the sulfur compounds. This concentrate was then treated with sodium aminoethoxide to extract thiols (mercaptans).

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[41] Haines, W. E., Helm, R. V., Bailey, C. W., and Ball, J. S., Purification and Properties of Ten Sulfur Compounds: Preprints, Div. Petrol. Chem., Am. Chem. Soc., September 14-19, 1952.

[42] Ball, J. S., Determination of Types of Sulfur Compounds in Petroleum Distillates: Bureau of Mines Rept. of Investigations 3591, 1941, 60 pp.

[43] Pharmocopea of the U. S. A., 8th ed., 1947, p. 782.

[44] Girelli, A., Relazioni Tra Numero di Atomi di Carbonio e Temperature di Ebollizione di Composti Solforati del Petrolio: La Rivista Dei Combustibili, vol. 7, No. 6, June 1953, pp. 3-8.

[45] Cattell, R. A., Petroleum and Natural Gas Research Program, Bureau of Mines, Fiscal Year 1952; Bureau of Mines Inf. Circ. 7659, 1953, p. 35.

This method of treatment[46] is outlined in figure 14, indicating that from 8,973 grams of 110°-150° C. distillate, representing about 7 percent of the original crude oil, 22.5 grams of thiol sulfur were obtained. This was recently fractionated, and the fractions were examined by infrared absorption spectroscopy. The following thiols were tentatively identified: 3-Methyl-2-butanethiol, 2-pentanethiol, 3-pentanethiol, 3-methyl-1-butanethiol, 2-methyl-1-butanethiol, 1-pentanethiol, cyclopentanethiol, 2-hexanethiol, 1-hexanethiol, and cyclohexanethiol. The method of extracting thiols from petroleum naphthas appears to be generally adaptable to higher boiling fractions and promises to be a useful procedure in identifying thiols in crude oil.

The extraction of cyclic sulfides from the thiol-free sulfur concentrate by zinc-chloride has been completed, and distillation analysis of the cyclic- and open-chain sulfide concentrates is underway. The efficiency of this extraction procedure does not appear to be as high as is the aminoethoxide extraction of thiols.

A preliminary paper reporting the identification of sulfur compounds found in Wasson, Tex., crude oil in boiling range 0° to 100° C. was published.[47] These compounds include all theoretically possible hydrogen-carbon-sulfur-containing compounds whose boiling points fall within this boiling range except the unstable C_2 and C_3 cyclic sulfides and their methyl derivatives and thiophene. The latter has never been authoritatively reported in crude oils.

The effect of heat upon sulfur-containing crude oils and distillates is important in both commercial processes and in various research techniques. This effect is of more importance now that it has been shown that some crude oils contain elemental sulfur. Some studies on the thermal stability of high-sulfur crude oils and low-sulfur oil with added sulfur or polysulfide were reported.[48] Figure 15 shows typical results with four different crude oils. In these figures the scale on the ordinate represents grams of sulfur evolved as hydrogen sulfide or volatile thiols. Of these crude oils, the Goldsmith oil contained over 1 percent of elemental sulfur, whereas the Wilmington oil had no elemental sulfur or thiols - only sulfides.

Thermal Decomposition of Sulfur Compounds

The reactions of sulfur compounds under the application of heat are interesting because of the widespread use of thermal processes in refining petroleum. To investigate them, pure sulfur compounds have been decomposed in a quartz tube utilizing a flow method. Temperatures and residence times were controlled, and the products were condensed and analyzed. The method has been described,[49] as well as

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[46] Hopkins, R. L., and Smith, H. M., Separation of Sulfur Compounds. 1. Extraction and Recovery of Thiols: Pres. Div. Petrol. Chem., Am. Chem. Soc., Los Angeles, Calif., Mar. 18, 1953.

[47] Ball, J. S., Bordwell, F. G., Smith, H. M., Waddington, Guy, and Seyfried, W. D., Synthesis, Properties, and Identification of Sulfur Compounds in Petroleum: Proc. API, vol. 32, No. 3, 1952, pp. 139-175.

[48] Coleman, H. J., Thompson, C. J., Rall, H. T., and Smith, H. M., Thermal Stability of High-Sulfur Crude Oils: Pres. Div. Petrol. Chem., Am. Chem. Soc., Los Angeles, Calif., Mar. 18, 1953; also in Ind. and Eng. Chem., vol. 45, No. 12, December 1953, pp. 2706-2710.

[49] Thompson, C. J., Meyer, R. A., and Ball, J. S., Thermal Decomposition of Sulfur Compounds. I. 2-Methyl-2-propanethiol. II. 1-Pentanethiol: Jour. Am. Chem. Soc., vol. 74, 1952, pp. 3284-3289.

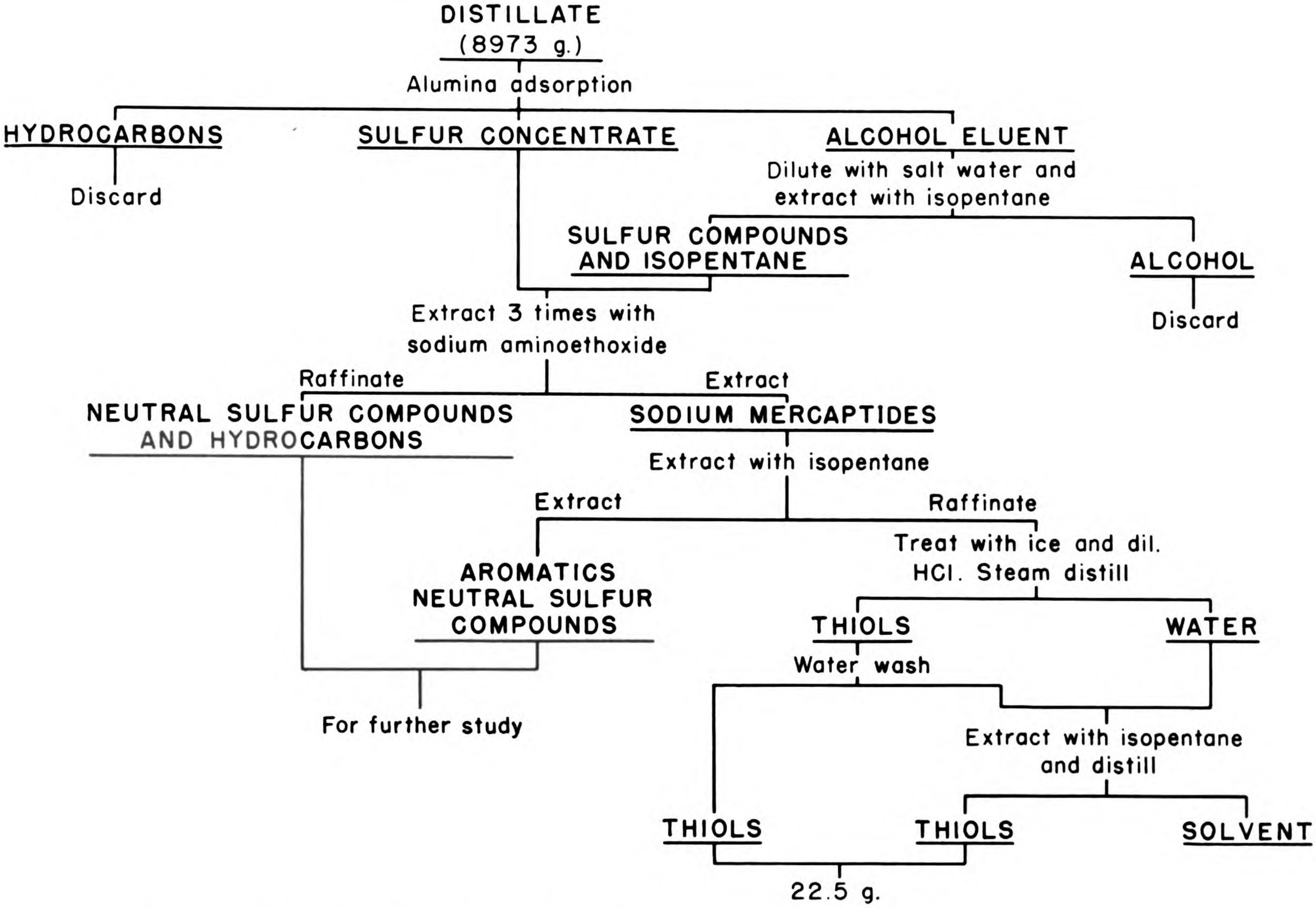
DISTILLATE
(8973 g.)
Alumina adsorption
HYDROCARBONS
Discard
SULFUR CONCENTRATE
ALCOHOL ELUENT
Dilute with salt water and extract with isopentane
SULFUR COMPOUNDS AND ISOPENTANE
ALCOHOL
Discard
Extract 3 times with sodium aminoethoxide
Raffinate
Extract
NEUTRAL SULFUR COMPOUNDS AND HYDROCARBONS
SODIUM MERCAPTIDES
Extract with isopentane
Extract
Raffinate
AROMATICS NEUTRAL SULFUR COMPOUNDS
Treat with ice and dil. HCl. Steam distill
THIOLS
WATER
Water wash
For further study
Extract with isopentane and distill
THIOLS
THIOLS
SOLVENT
22.5 g.

Figure 14. - Treatment of 111° to 150° C. boiling range Wasson distillate to obtain thiol concentrate.

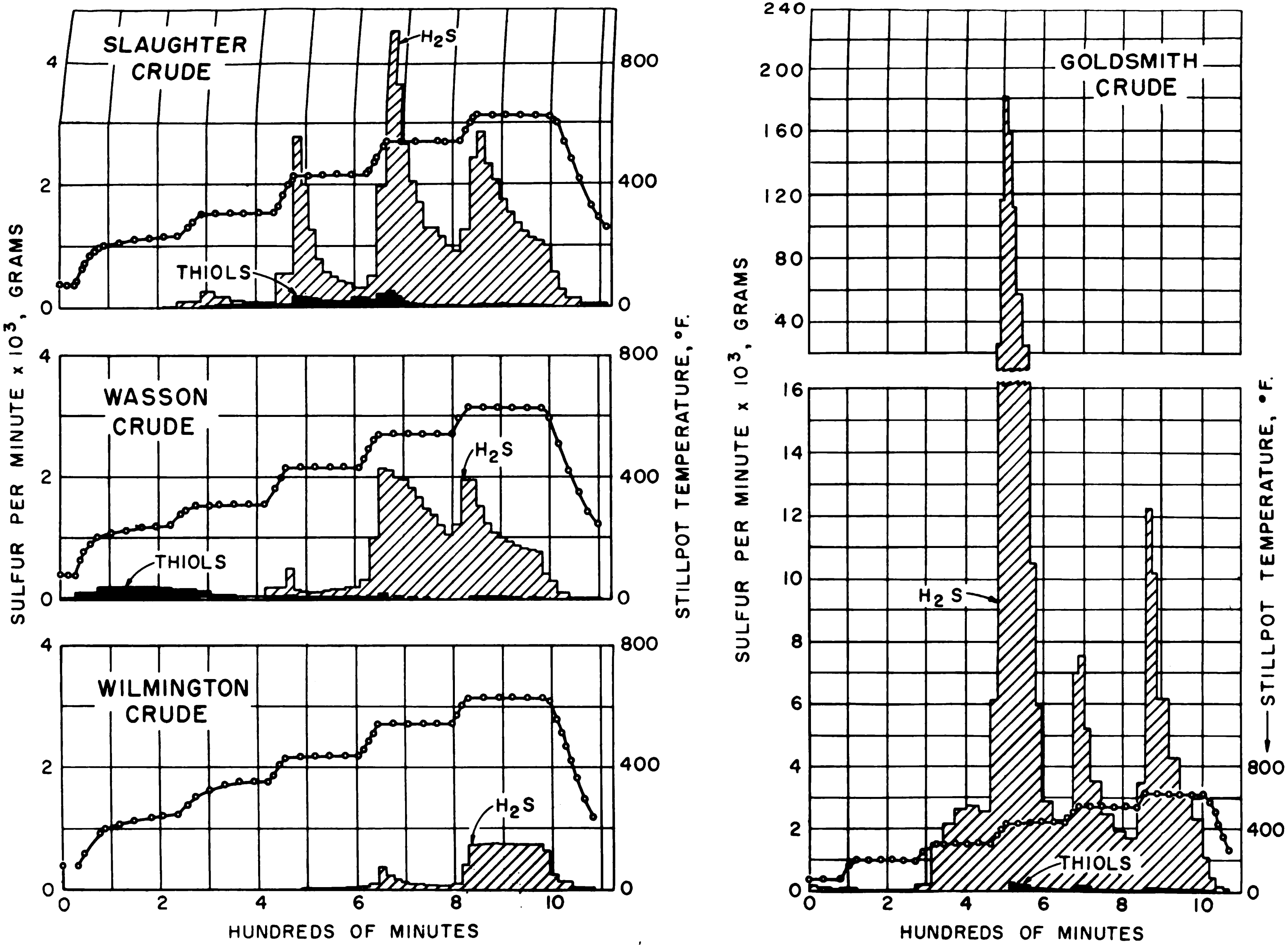

Figure 15. - Thermal stability test of various high-sulfur crude oils.

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results on 1-pentanethiol and 2-methyl-2-propanethiol. Inasmuch as these are primary and tertiary thiols, results on a secondary thiol are necessary to complete the series. The data on this compound show that the primary products of the overall reaction are the same as with the two thiols previously studied, that is, hydrogen sulfide and the corresponding olefin. The reaction mechanism is postulated as being largely free radical and similar to that already suggested for 2-methyl-2-propanethiol. Again, as with 2-methyl-2-propanethiol, an induction period was observed at the lower operating temperatures. Rate data have been developed and are being prepared for publication.

Nitrogen Compounds in Distillate Fuels

A systematic method for types of nitrogen compounds was devised by combining previously published methods for total nitrogen, basic nitrogen, and pyrrole nitrogen. This method was used on 34 samples of diesel fuel oil undergoing stability testing. The results were presented before the American Chemical Society and published.50/

Nitrogen compounds are thought to cause the instability of certain distillate fuels. It was thought that correlations between the types of nitrogen compounds present and the instability of the fuels might be developed. When the stability-testing program was set up in cooperation with the Western Petroleum Refiners Association, the Bureau of Ships was interested in developing these correlations and provided funds for the study of the nitrogen compounds.

Besides the systematic analysis mentioned previously, experiments to concentrate the nitrogen compounds (approximately 1 percent of the fuel) have shown that adsorption on florisil accomplishes this. A thermally cracked diesel fuel was concentrated in this manner. Various separation techniques have been tested for separating the nitrogen compounds into classes.

The possible presence of porphyrins in the nitrogen concentrate was investigated. Through synthesis of a porphyrin and testing of a synthetic mixture containing the porphyrin, it was established that the florisil treatment removed porphyrins. Analysis of the concentrate from the thermally cracked fuel showed no porphyrin. Concentrates from straight-run and catalytically cracked fuels are to be made and tested for porphyrins.

Chemical Studies of Fuels

Gasoline

Data obtained in Bureau of Mines studies of the composition of aviation gasoline base stocks from many different crude oils from 1940 to 1945 provided an opportunity to compare the compositions of base stocks from different sources. An interesting comparison showed that the ratios of certain hydrocarbons present in different base stocks was surprisingly constant. Ratios of hydrocarbons in the range from 6 to 9 carbon atoms from 21 base stocks from domestic crude oils and 11 foreign crude oils were published during the past year.51/

50/ Ward, L. F., Jr., Moore, R. T., and Ball, J. S., Nitrogen Compounds in Distillate Fuels: Anal. Chem., vol. 25, 1953, pp. 1070-1072.

51/ Smith, H. M., and Rall, H. T., Relationship of Hydrocarbons With Six to Nine Carbon Atoms: Ind. Eng. Chem., vol. 45, No. 7, 1953, pp. 1491-1497.

Diesel Fuel

Greatly increased demands for distillate fuels have forced some refiners to blend substantial quantities of catalytically cracked stocks with straight-run stocks to extend their fuel supplies. Unfortunately, catalytically cracked fuels are somewhat less stable than straight-run stocks, and furthermore some catalytically cracked stocks and straight-run stocks are not compatible. A mixture of such stocks form a gum or precipitate in storage that plugs the filters and injectors of diesel engines. This problem became so serious and widespread in the industry that the Western Petroleum Refiners Association and the Bureau of Mines entered into a cooperative agreement to study the fundamental causes of instability and incompatibility. The study was organized with two objectives: (1) To make a comprehensive laboratory study of representative distillates under a variety of storage conditions identically imposed; (2) to determine the causes of the phenomena that result in instability and incompatibility. Under the first part of this program 34 fuels, which include straight-run, catalytically cracked, and thermally cracked distillates, were obtained from refiners. The crude-oil sources of these fuels represented the major producing areas of the United States and several foreign fields. Samples of these 34 fuels and 69 blends of fuels were stored in vented 1-pint bottles at 110° F. One series of samples had no contaminant and others contained iron and water, copper, copper and seawater, iron, and galvanized iron and seawater. The effect of storage condition on deterioration as measured by insoluble gum formation in a straight-run, a catalytically cracked, and a thermally cracked fuel is shown in figure 16.

Of the 60 blends that were stored, 27 showed incompatibility in that the determined value for gum content was higher than would be anticipated from the amount of gum formed in the unblended components under the same conditions. This is illustrated in figure 17, which shows the amount of insoluble gum in a 50-50 blend of a straight-run fuel and a catalytically cracked fuel. The amount of gum formed in the unblended straight-run fuel at the same storage conditions for the same period is indicated by the height of the cross-hatched bar and that of the catalytically cracked fuel by the diagonally hatched bar. The average of the two is shown by the horizontal line, and the determined value of the blend is shown by the black bar. The amount of gum represented by the difference between the horizontal line and the black bar is the result of incompatibility.

The accelerated ageing of fuels with selected catalysts is suitable for a research program, but from a practical point of view, it is necessary to relate these results to those that occur in steel drums or tanks at atmospheric temperatures. In order to obtain such a correlation, 24 of the 34 fuels used in the laboratory storage program were stored in vented 55-gallon drums in an open shed. Figure 18 shows a comparison of soluble gum formed in fuels stored in bottles for 13 weeks at 110° F. and for the same fuels in drums at ambient temperature for 12 months. The 45° dashed line is shown for comparison of the actual curve and perfect correlation.

The substitution of catalytically cracked distillates for straight-run distillates in diesel fuels has posed another problem in that catalytically cracked fuels have inherently lower cetane numbers than straight-run distillates. A number of ignition improvers have been proposed to upgrade these type fuels. Fuels sometimes are stored for a year or more before use, and the question is naturally raised as to whether these additives retain their ignition improving quality and how they affect the soluble and insoluble gum formation. In order to give a partial answer to these questions, 12 catalytically cracked distillates were stored with 0.2 and 0.5 percent by volume of a commercially available ignition improver, amyl nitrate. Figure 19 shows that the amyl nitrate in storage for 13 weeks at 110° F. retains its

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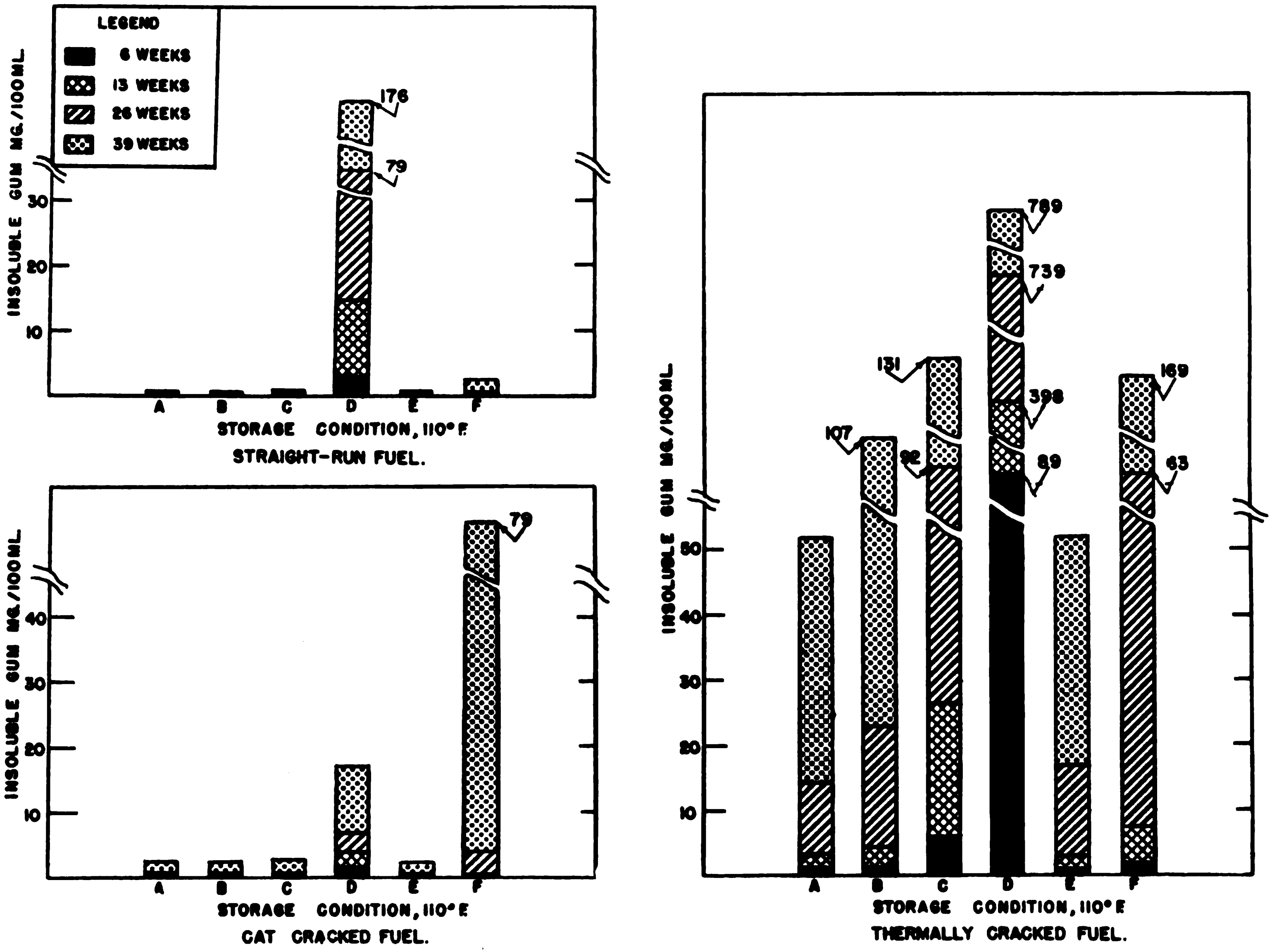

Figure 16. - Insoluble gum formed in a straight-run, a catalytically cracked, and a thermally cracked fuel with various contaminants during 4 storage periods at 110° F.

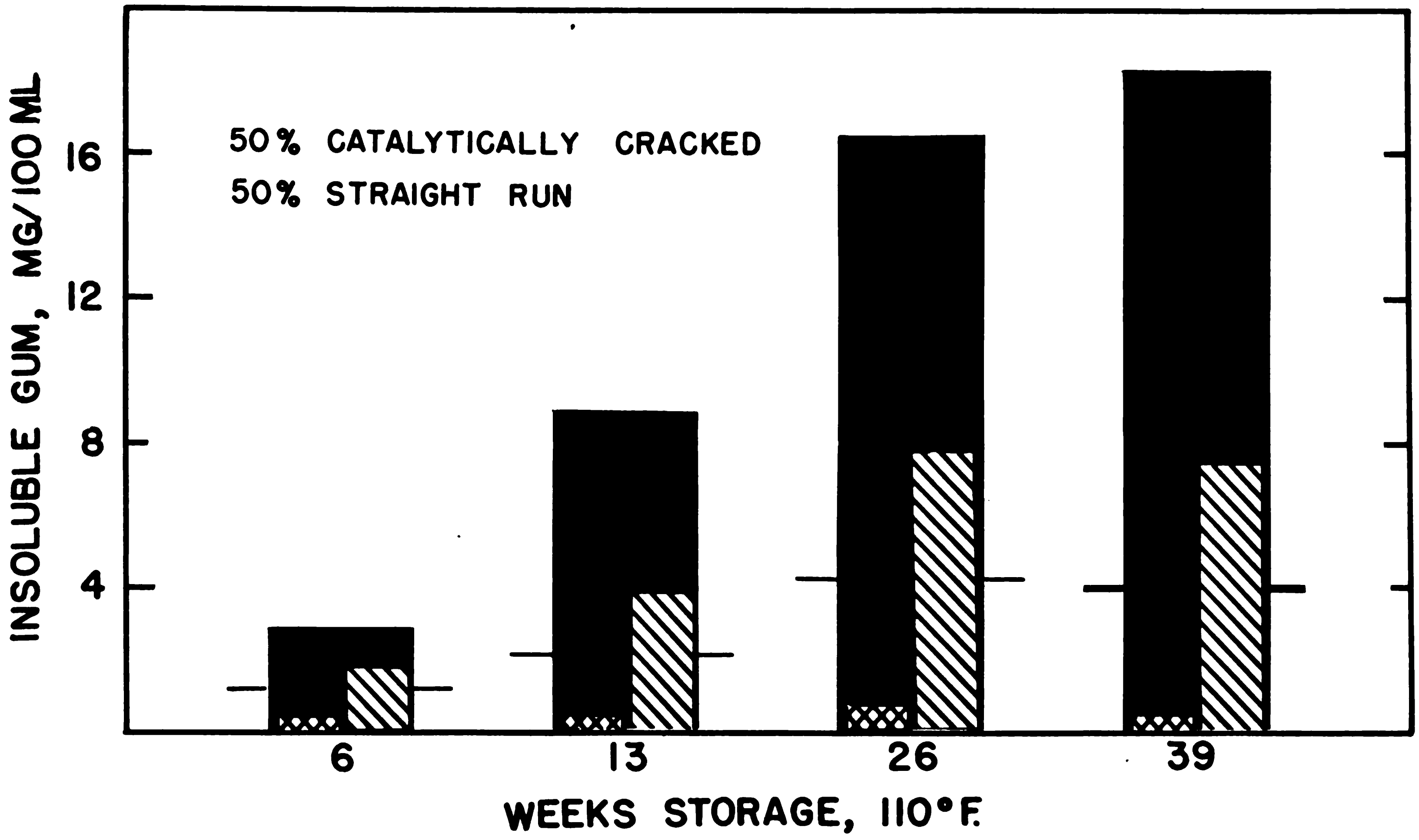

Figure 17. - Comparison of calculated and determined insoluble gum values in a binary blend of highly incompatible fuels.

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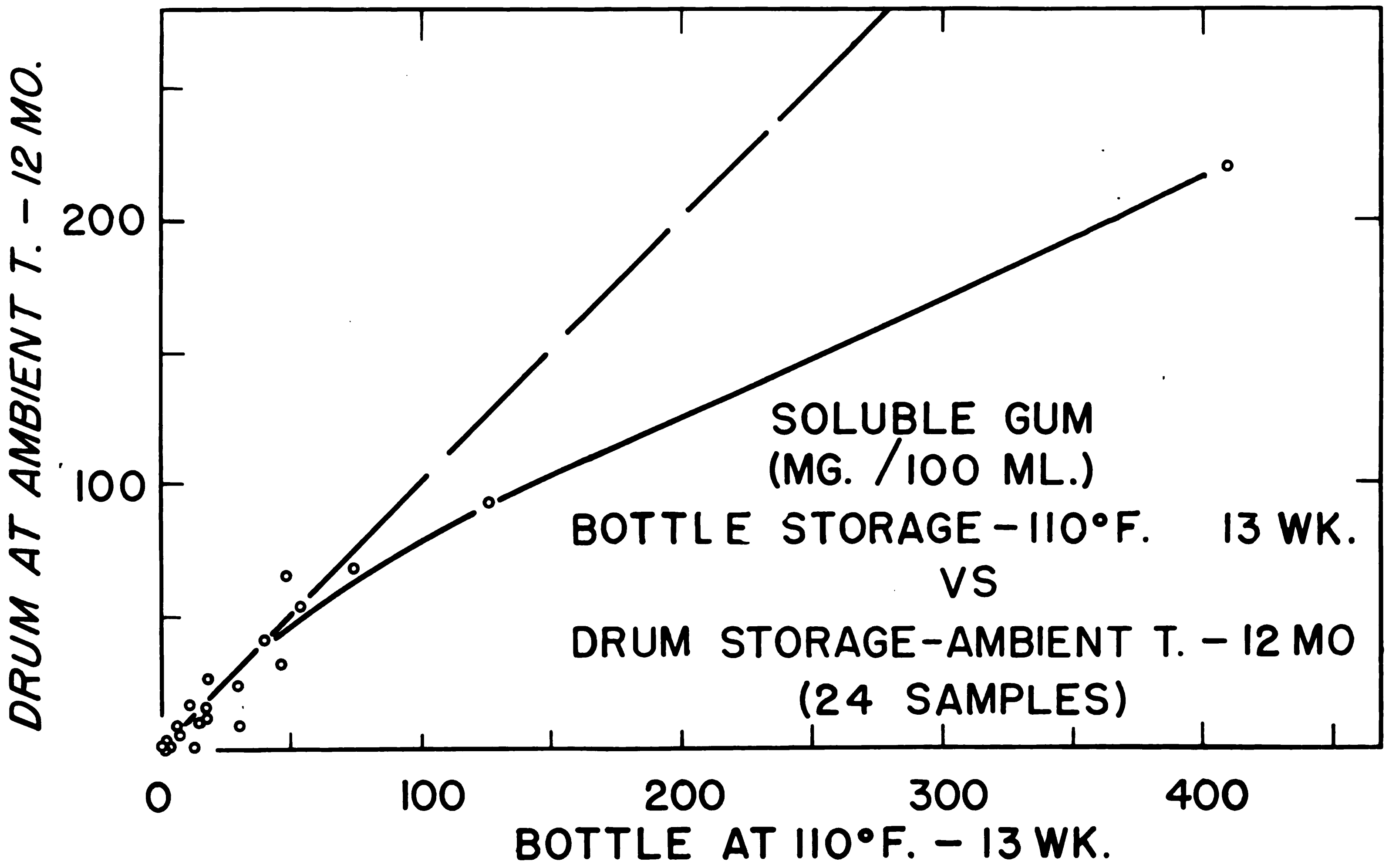

Figure 18. - Comparison of soluble gum formed in fuels in bottles at 110° F. and in drums at ambient temperature.

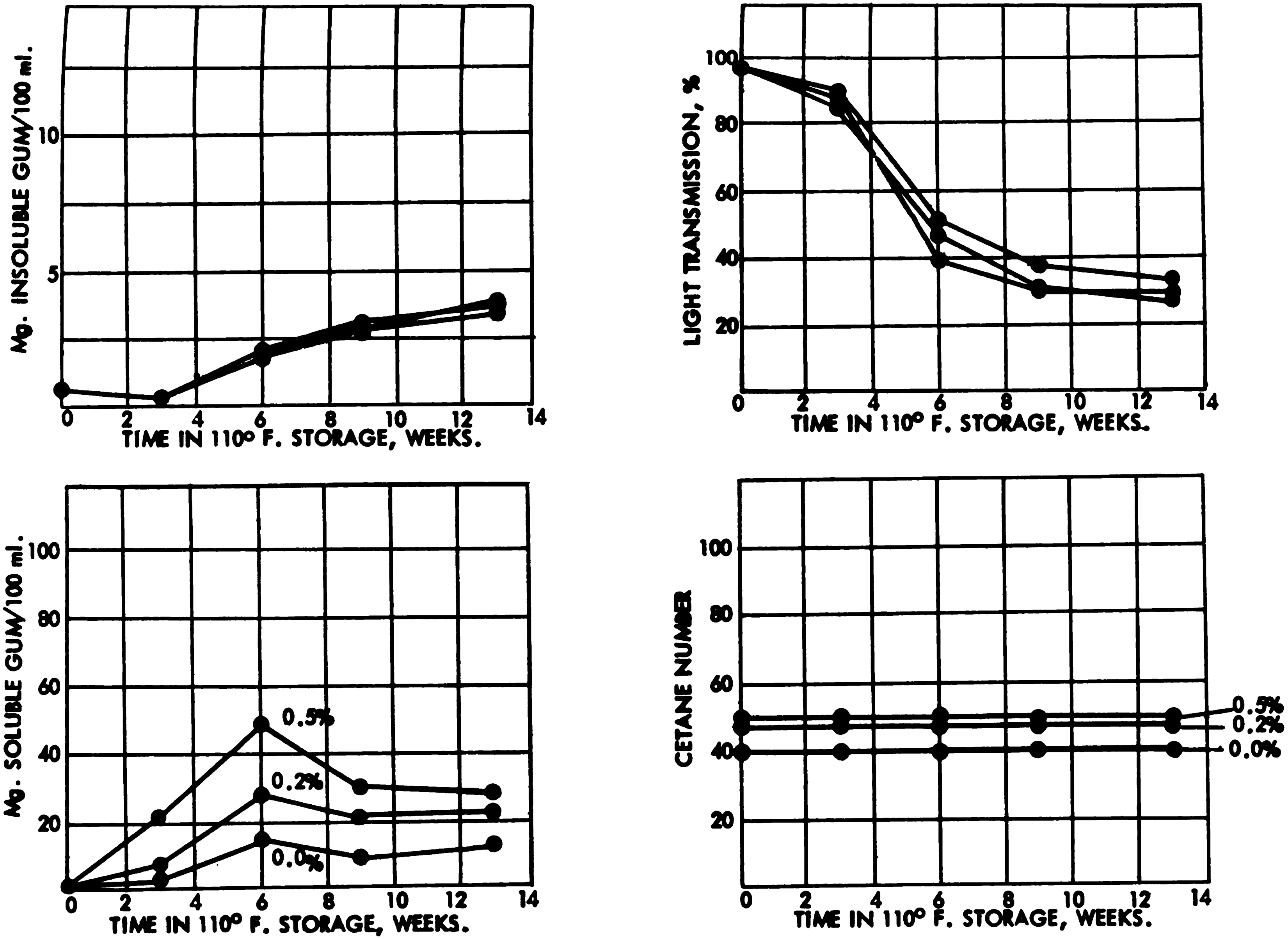

Figure 19. - Effect of amylnitrate on significant properties of a catalytically cracked diesel fuel during storage.

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ignition-improving quality, has little effect on insoluble gum or color, and results in a slight increase in soluble gum content.

As an approach to the fundamental causes for instability and incompatibility of distillate fuels, studies are being made of hydrocarbon composition of the fuels, oxygen susceptibility, sulfur and nitrogen compounds, trace metals, analyses of soluble and insoluble gum, and polar compounds. Data now available from these studies are promising, but a great deal more work will be required before any firm conclusions can be reached.

Continuing the investigation of close-cut fractions of West Edmond crude oil, biphenyl and 3-methyl biphenyl were identified[52] in the 241° and 262° C. boiling-point fractions, respectively, from a West Edmond distillate. Figure 20 shows the infrared spectra of biphenyl and 3-methylbiphenyl as isolated from the crude oil and as prepared from commercial sources of these two compounds. The close agreement of the spectrum of the synthetic compound with that isolated from the crude oil is proof of identity. Ultraviolet spectra (not shown) also point to identity. The slight discrepancy in match between the synthetic and isolated 3-methyl biphenyl, particularly at 12.20 microns, is caused by the presence in the 3-methyl biphenyl isolated from the crude oil of a small amount of 4-methyl biphenyl. This work establishes the presence of this class of compounds in crude oils.

Combustion Research on Fuels

Constant-Volume Bomb

Two of the constant-volume combustion bomb units were in operation throughout the year. One unit was devoted solely to work under contract with the U. S. Navy, and the second unit was used principally for investigations made in cooperation with the Coordinating Research Council, which supported the work by grants from the Internal Combustion Engine Institute and the American Petroleum Institute.

The Navy contract work was laid out as a fundamental type investigation to determine the influence of inert gases and water vapor on the combustion of a commercial type diesel fuel under conditions promoting auto-ignition.

To meet an urgent need for a means of determining the oxidation susceptibility of lubricants under highly oxidizing conditions, a bomb unit was hastily modified for use of 100-percent oxygen, and the necessary oxidation susceptibility information was successfully obtained within 90 days.

The industry cooperative work included studies of a series of fuels used in full-scale railroad fuel tests and another series of fuels tested in a number of industry laboratories to determine the importance or significance of front-end volatility in diesel fuels. These bomb data were obtained to supplement engine data and provide a basis for more comprehensive evaluation of the reasons for observed combustion behavior. Results of these studies are being prepared for publication.

Determination of the ignition characteristics of pure hydrocarbons in the diesel range was resumed in early 1953.

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[52] Adams, N. G. and Richardson, D. M., Isolation and Identification of Biphenyls From West Edmond Crude Oil: Anal. Chem., vol. 25, 1953, pp. 1073-1074.

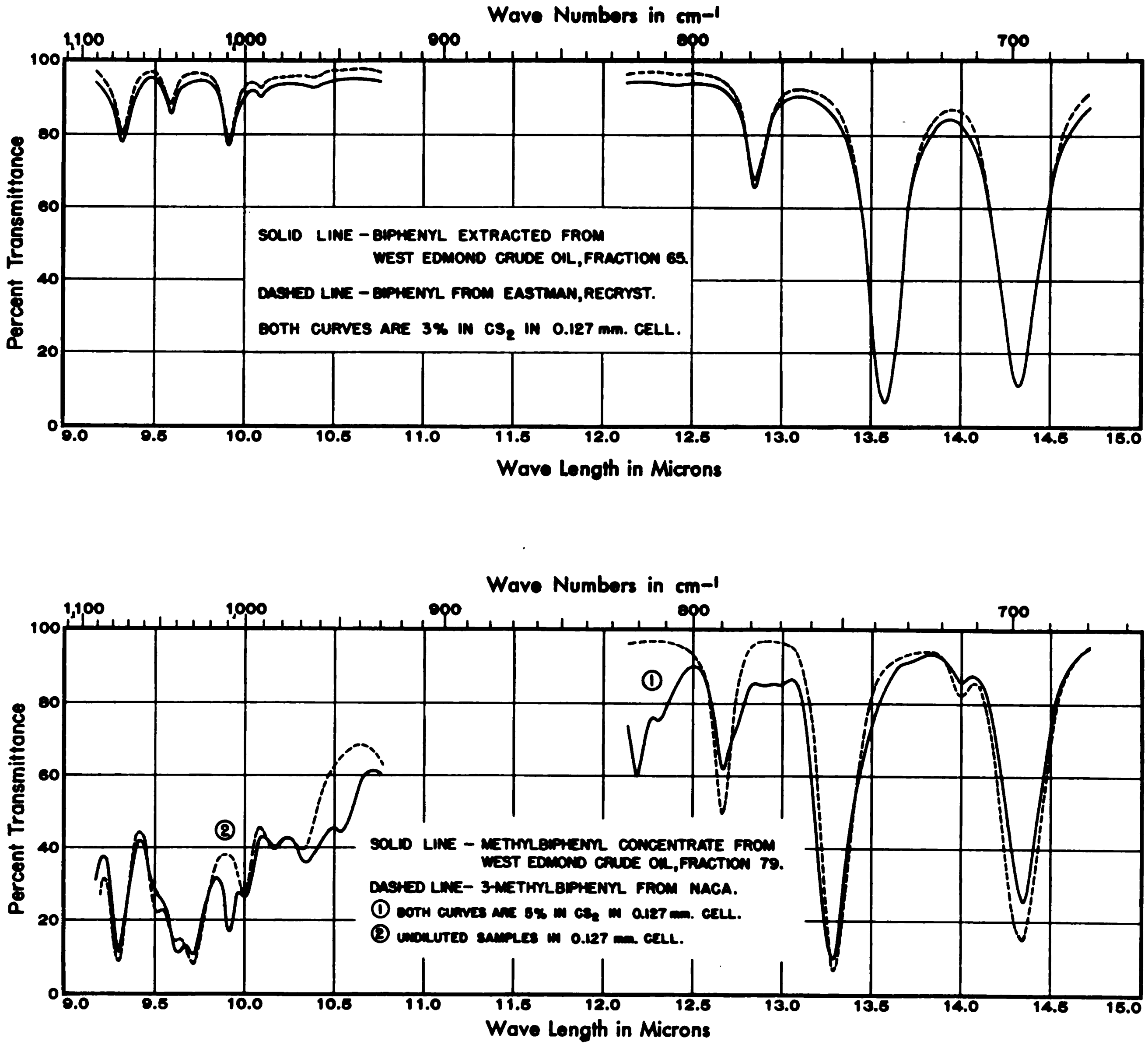

Figure 20. - Comparison of infrared spectra of concentrates from West Edmond crude oil with those of pure biphenyls.

Engine Studies

Four fuels having widely different volatility ranges were tested in the research diesel unit to obtain information for use in correlating bomb data with engine test results. These same fuels are currently being tested in industry laboratories, and correlation studies will be made when all data are available.

Composition and Properties of Petroleum Asphalt

Asphalt investigations during the past year were a continuation of a project begun in 1951 to evaluate petroleum asphalt by determining the amounts and types of its hydrocarbon components. The initial asphaltene and petrolene fractions from 600 grams of a 105-penetration asphalt from Oregon Basin, Wyo., were subjected to extensive fractionation, chiefly by solvent extraction, into groups of components for future analysis and characterization.

Fractionation of the initial crude asphaltenes (21.9 percent of the asphalt) was completed. This involved successive Soxhlet extractions for a total of approximately 1,500 hours and yielded 10.94 percent of n-pentane-soluble material, 11.17 percent diethyl ether-soluble material, 19.36 percent methyl tertiary amyl ether-soluble material, and 61.87 percent benzene-soluble material.

Fractionation of the initial crude petrolenes (78.1 percent of the asphalt) was partly completed. This involved extraction of the petrolenes with n-butanol at 122° and 6° to 10° F. Two of these butanol fractions were extracted with acetone, then with methyl ethyl ketone at temperatures of -10° and 0° F., respectively. Preparation of urea adducts from some of the fractions was used to separate straight-chain paraffin hydrocarbons, but an attempt to prepare hydrocarbon complexes with trinitrofluorenone was unsuccessful. For the most part, physical and chemical properties of the asphalt fractions have not been determined.

Fuel Surveys

Four reports were published during the fiscal year showing results of surveys on motor gasolines for: The winter 1951-52 and summer 1952,53/ aviation gasoline and jet fuel, 1952 production,54/ and diesel fuel produced in 1952.55/ In addition, a report on motor gasolines for winter 1952-53 was prepared during the fiscal year and appeared in July 1953.56/ A feature of motor-gasoline surveys is the indicated trend to higher octane numbers. On figure 21 are shown trend-charts of the research

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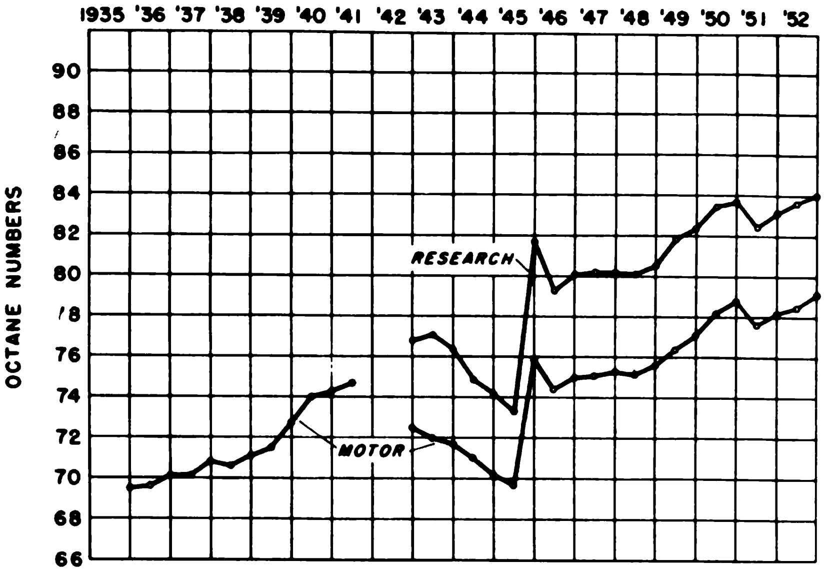
53/ Blade, O. C., National Motor-Gasoline Survey, Winter 1951-52: Bureau of Mines Rept. of Investigations 4901, 1952, 24 pp.; National Motor-Gasoline Survey, Winter 1951-52: Oil Gas Jour., Aug. 4, 1952, p. 95.
_____. National Motor-Gasoline Survey, Summer 1952: Bureau of Mines Rept. of Investigations 4963, 1953, 24 pp.

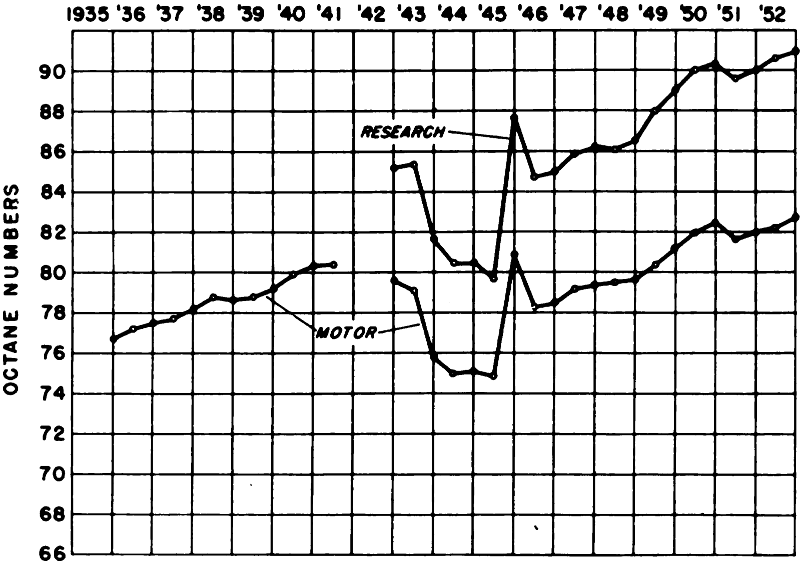
54/ Blade, O. C., National Annual Survey of Aviation Gasoline and Aviation Jet Fuel, 1952 Production: Bureau of Mines Rept. of Investigations 4982, 1953, 15 pp. Aviation Fuels - 1952 Production: Oil Gas Jour., July 6, p. 95.

55/ Blade, O. C. National Annual Diesel-Fuel Survey, 1952: Bureau of Mines Rept. of Investigations 4935, December 1952, 22 pp. Annual Diesel-Fuel Survey - 1952: Oil Gas Jour., Feb. 16, 1953, pp. 154, 156.

56/ Blade, O. C., National Motor-Gasoline Survey, Winter 1952-53: Bureau of Mines Rept. of Investigations 5000, 1953, 24 pp.



REGULAR—PRICE GASOLINE



PREMIUM—PRICE GASOLINE

Figure 21. - Trends of octane numbers of motor gasolines in the United States.

and motor-method octane numbers for regular-price and premium-price motor fuels based on national average figures computed in the surveys. New record values are:

	Octane numbers, winter 1952-53	
	Research method	Motor method
Regular-price gasolines	84.0	79.1
Premium-price gasolines	90.9	82.7

The diesel-fuel survey report differed from those of 1950 and 1951 in that the analytical data were arranged in groups to represent samples, in their respective grades, according to major distribution in five geographic regions of the country. Analyses of fuels of minor distribution in other regions were repeated, where necessary, to complete the geographic representation of the diesel fuels sold.

These surveys on motor gasolines, aviation fuels, and diesel fuels are conducted under a cooperative agreement between the United States Department of the Interior, Bureau of Mines, and the American Petroleum Institute. By this agreement samples of the fuels are analyzed in the laboratories of oil, chemical, and motor companies by standard methods and the results transmitted to the Bureau of Mines for compilation and publication. The reports are used by refiners of petroleum, chemical and engine manufacturers, State and Federal inspectors, and consumers. The reports are also in demand by committees on specifications who use the data in various ways in their studies of fuel quality.

THERMODYNAMICS OF PETROLEUM

Advances in petroleum technology depend on an evergrowing knowledge of the hundreds of substances present in crude oil and the useful products made from it. As science has focussed attention on these individual chemical compounds and measured their properties, it has been possible for petroleum refining to advance from empirical, rule of thumb methods to efficiently controlled processes. The chemical thermodynamic properties rank high among the several kinds of properties of these compounds for which accurate knowledge is essential to technical progress. A generation ago, virtually nothing was known of the chemical thermodynamic properties of petroleum hydrocarbons or their derivatives. In the intervening years, through improved experimental methods and theoretical approaches, knowledge of these properties has grown to an impressive extent. For most of the simpler hydrocarbons of natural gas and petroleum, accurate thermodynamic information is now available. But the fund of thermodynamic information should keep pace with the mounting demands of petroleum technology and expand to include more complex hydrocarbons, substances unique to lower grade raw materials, such as high-sulfur crude oils and shale oil, and the host of useful derivatives met in the rapidly growing petrochemical industry.

In the Thermodynamics Laboratory at Bartlesville, Okla., the Bureau of Mines conducts a research program designed to provide thermodynamic data required by chemists and engineers concerned with research and chemical process design in the petroleum and petrochemical industries. The current program of this laboratory, which reflects closely the present interests of industry, may be divided into the following sub-programs: (1) Studies of the thermodynamic properties of pure hydrocarbons. The Thermodynamics Laboratory has made an important contribution to the knowledge of the properties of hydrocarbons of the types found in gasoline. Similar studies are now in progress on some of the constituents of diesel and jet fuels. (2) A systematic study, conducted in cooperation with American Petroleum Institute Research Project 48A, of the thermodynamic properties of sulfur compounds important to the petroleum industry. This work is designed to give information that will be needed to develop new methods for manufacturing useful sulfur compounds and eliminating harmful or obnoxious products from petroleum fuels. At the end of the fifth year of research in this field, the goal is now in sight of having complete thermodynamic data for several of the most common types of sulfur compounds. (3) Studies of halogen- and oxygen-containing compounds. Some valuable work has been completed in these fields, and it is hoped to expand this program to aid the research workers of the petrochemical industry. (4) Studies of individual compounds or groups of compounds of unique interest. At the request of other governmental agencies or industrial groups, more specialized studies are made of compounds that are important to defense requirements or are of general interest to industry. In cooperation with Air Research and Development Command, the Thermodynamics Laboratory is now determining certain properties of fluorocarbons, a new and important group of petrochemicals.

The primary objective of these thermodynamic investigations is to provide information that will make it possible to calculate the yields of chemical processes, the temperatures and pressures at which industrial processes can best be carried out, and the temperatures at which a compound may be expected to decompose. To make such calculations, it is necessary to have values of two important chemical thermodynamic properties, the entropy and the heat of formation. The following experimental and computational projects have been designed to meet these objectives: (1) Determination of the heat capacity and other thermal properties from about -440° to about +200° F. From the results of these studies, the entropy of a compound in the solid and liquid states may be derived. (2) Determination of the heat of combustion, from which the heat of formation at room temperature of a liquid or solid compound may be computed. (3) Measurements of the heat of vaporization and the heat capacity of the vapor. Using these data and values of the entropy and heat of formation of the liquid or solid, values of the entropy and heat of formation of the vapor may be computed at temperatures up to 500° F. These thermodynamic data for the vapor are the most valuable for use in chemical process design. (4) Studies of the vapor-liquid equilibria at high and low pressures. The data obtained in this project are used in interpreting the data obtained in the first three projects and also in extending the experimental data to the high pressures required in actual chemical processes. (5) Statistical mechanical calculations of the thermodynamic properties. The thermodynamic properties of a compound are computed by theoretical methods on the basis of spectroscopic data, molecular-structure information, and the experimental thermodynamic data. This calculation program not only correlates and puts into a more useful form all of the experimental data but also extends the calorimetric results to higher temperatures at which experimental measurements are impractical. In many cases, research and process design in the petroleum field requires thermodynamic information at these higher temperatures.

In addition to providing values of the heat of formation and entropy, the thermodynamics program also yields certain other thermal data, for example, heat capacities, heats of fusion, vaporization, combustion, and boiling points and melting points, which are necessary for the efficient design of large-scale refinery equipment.

Accomplishments during 1953 in each of the fields of investigation mentioned above are discussed in the following sections.

Low-Temperature Calorimetry

In 1953, studies were made of the low-temperature thermal properties of 10 compounds, of which 4 were hydrocarbons and 6 were sulfur compounds. The hydrocarbons

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studied, 1-undecene, 1-dodecene, 1-methylnaphthalene, and cycloheptatriene, are illustrative of the fact that thermodynamic data are now lacking only for the more complex hydrocarbon compounds that may occur in petroleum or refinery streams. The studies of the first two compounds, 1-undecene and 1-dodecene, nearly complete an extensive series of investigations of an important family of hydrocarbons, the 1-olefin compounds. The study of 1-methylnaphthalene is the first in a series of investigations of naphthalene and its derivatives. Both of these series of investigations are being conducted at the request of American Petroleum Institute Research Project 44. They are similar to studies already completed of the families of normal paraffin hydrocarbons[57] and alkylcyclopentanes.[58]

The following sulfur compounds were studied as part of American Petroleum Institute Research Project 48A: 1-butanethiol, 2-thiapentane, 4-thiaheptane, thiacyclohexane, 2-methylthiophene, and 3-methylthiophene.[59] These compounds are representative of most of the types of sulfur compounds that are known to occur in crude petroleum.

Combustion Calorimetry

After a period of difficult design and development work, a rotating-bomb combustion calorimeter was developed for determining with high accuracy the heats of combustion and formation of organic sulfur compounds.[60] In 1953, the heats of combustion and formation of thiacyclobutane,[61] 3-methylthiophene, thiacyclohexane, and thianthrene were determined with an accuracy comparable to that of the best existing data for hydrocarbons. During these investigations, significant progress was made in the continuing efforts to arrive at the best techniques for this new experimental method. Since the rotating-bomb method for sulfur compounds represents a new and unique tool for precise thermochemical measurements, it has been necessary to devote considerable time to establishing the reliability of the method. Manuscripts describing the apparatus and method, the evaluation of the method, the experimental data obtained,[60] and the theoretical interpretation of the data[62] have been prepared in order that other chemists may adopt the method for their research work.

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[57] Finke, H. L., Gross, M. E., Waddington, Guy, and Huffman, H. M., Low-Temperature Thermal Data for the Nine Normal Paraffin Hydrocarbons From Octane to Hexadecane: Jour. Am. Chem. Soc., vol. 76, No. 2, Jan. 20, 1954, pp. 333-341.

[58] Gross, M. E., Oliver, G. D., and Huffman, H. M., Low-Temperature Thermal Data for Some C_7H_{14} Alkylcyclopentanes: Jour. Am. Chem. Soc., vol. 75, No. 12, June 20, 1953, pp. 2801-2804.

[59] McCullough, J. P., Sunner, S., Finke, H. L., Hubbard, W. N., Gross, M. E., Pennington, R. E., Messerly, J. F., Good, W. D., Waddington, Guy. The Chemical Thermodynamic Properties of 3-Methylthiophene from 0 to 1,000° K.: Jour. Am. Chem. Soc., vol. 75, No. 20, Oct. 20, 1953, pp. 5075-5081.

[60] Hubbard, W. N., Katz, C., and Waddington, Guy, A Rotating Combustion-Bomb for Precision Calorimetry. Heats of Combustion of Some Sulfur-Containing Compounds: Jour. Phys. Chem., vol. 58, No. 2, February 1954, pp. 142-153.

[61] Scott, D. W., Finke, H. L., Hubbard, W. N., McCullough, J. P., Katz, C., Gross, M. E., Messerly, J. F., Pennington, R. E., and Waddington, Guy, Thiacyclobutane: Heat Capacity, Heats of Transition, Fusion and Vaporization, Vapor Pressure, Entropy, Heat of Formation and Thermodynamic Function: Jour. Am. Chem. Soc., vol. 75, No. 12, June 20, 1953, pp. 2795-2800.

[62] Hubbard, W. N., Scott, D. W., and Waddington, Guy, Reduction to Standard States (at 25°) of Bomb Calorimetric Data for Compounds of Carbon, Hydrogen, Oxygen, and Sulfur: Jour. Phys. Chem., vol. 58, No. 2, February 1954, pp. 152-162.

Many of the essential details of the rotating-bomb method were presented orally to interested chemists at the meetings of the American Chemical Society and the Calorimetry Conference, both held in Atlantic City in September 1952.

Construction of a second, improved rotating-bomb calorimetric system was completed, and preliminary tests of the equipment have been made. This second apparatus will be used to determine the heat of combustion of lead tetraethyl, under a cooperative agreement with one of the leading producers of that antiknock compound, and for determining the heats of combustion of several fluorocarbons, under contract with the Air Research and Development Command. The versatility of the rotating-bomb method is illustrated by its use with these different types of compounds, all of which are important to large segments of the petroleum industry.

The heats of combustion and formation of tropolone63/ were determined by conventional, static-bomb calorimetric methods. This study was undertaken to provide information concerning the molecular structure of this seven-membered ring compound. Seven- and eight-membered ring structures have recently become of interest to the petroleum and chemical industries.

The Commission on Thermochemistry of the International Union of Pure and Applied Chemistry has requested the staff of this laboratory to write or assist in writing six chapters for a book on Experimental Thermochemistry. These chapters have been completed and submitted to the editor of the book.

Vapor-Heat Capacity and Heat of Vaporization

Through a continuing series of modifications and improvements of the flow-calorimetric system, the versatility and efficiency of this unique apparatus for measuring the vapor-heat capacity and heat of vaporization have been greatly increased. The properties of six compounds were measured in the last year. Of these compounds, four were sulfur compounds typical of those found in crude petroleum - thiacyclohexane, 2-butanethiol, 2-methylthiophene, and 3-methyl-2-thiabutane. Measurements were made of the vapor-heat capacity and heat of vaporization of the hydrocarbon, 1,trans-3-dimethylcyclopentane. These flow-calorimetric data previously determined data for cyclopentane and methylcyclopentane (unpublished), and the low-temperature data for several alkylcyclopentanes mentioned above58/ will provide a sound basis for compiling tables of thermodynamic functions for one of the important constituent families of petroleum compounds.

Previously determined data for water were recently published in a technical journal.64/ This investigation served not only to establish further the reliability of the experimental methods used to measure vapor-heat capacities and heats of vaporization, but also provided valuable new data for this important industrial compound. It is noteworthy that, although the properties of water have been more extensively studied than those of any other compound, significant unique contributions to the knowledge of its properties can be made by using methods developed in this laboratory.

63/ Hubbard, W. N., Katz, C., Guthrie, G. B., Jr., and Waddington, Guy, The Heat of Combustion and Resonance Energy of Tropolone: Jour. Am. Chem. Soc., vol. 74, No. 17, Sept. 5, 1952, pp. 4456-4458.

64/ McCullough, J. P., Pennington, R. E., and Waddington, Guy, A Calorimetric Determination of the Vapor Heat Capacity and Gas Imperfection of Water: Jour. Am. Chem. Soc., vol. 74, No. 17, Sept. 5, 1952, pp. 4439-4442.

Pressure-Volume-Temperature and Vapor-Liquid Equilibrium Studies

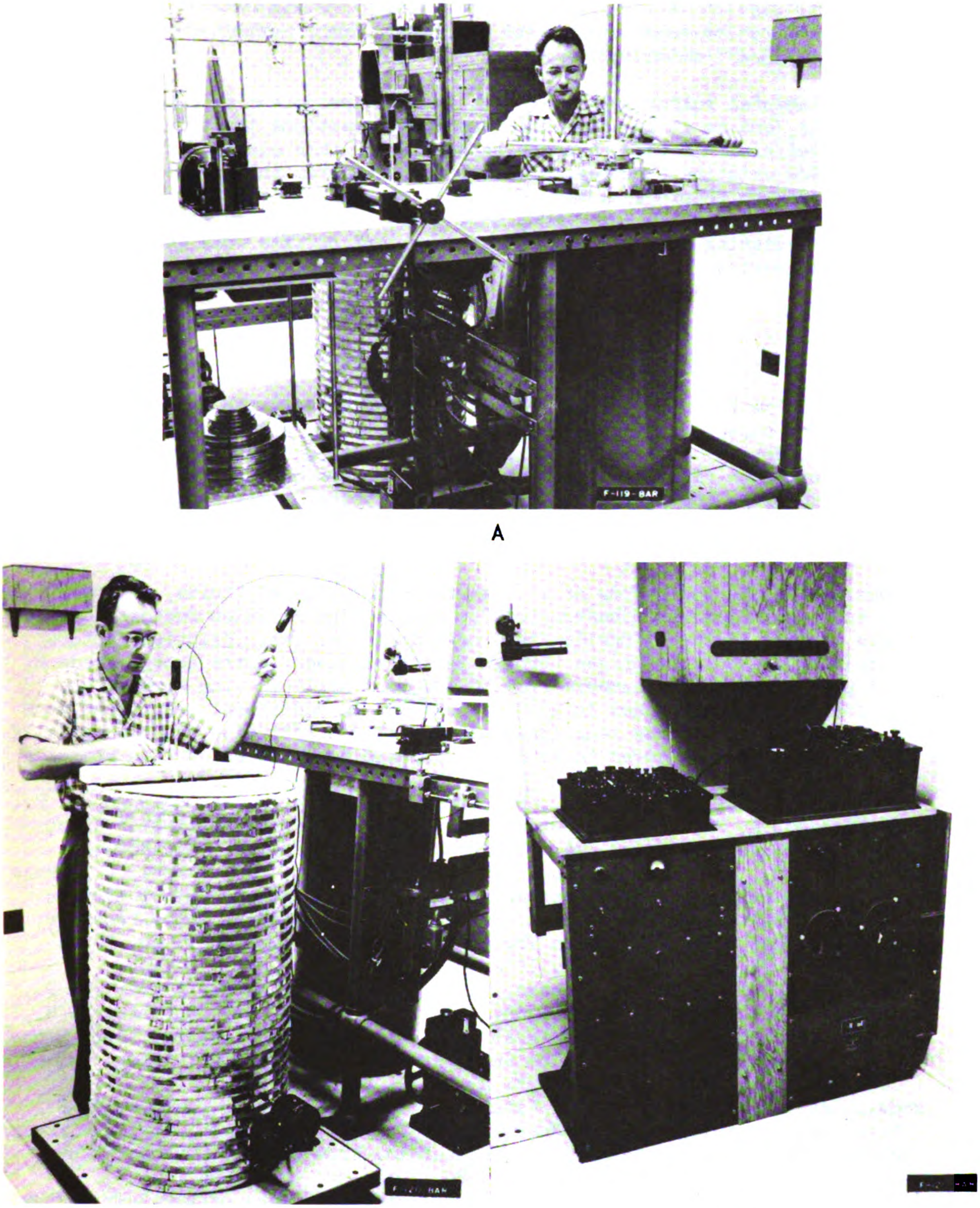
Pressure-volume-temperature (P-V-T) and vapor-liquid equilibrium studies constitute an essential part of a balanced thermodynamic program in three major ways: First, the reactivity of compounds in high-pressure chemical processes can be calculated from known low-pressure data if the P-V-T properties of the compounds involved in the reaction have been determined; second, equipment for separating and purifying finished products from chemical processes may be designed more efficiently if the phase equilibrium relationships are known to process-design engineers; and third, the theoretical information about intermolecular forces and intermolecular behavior that can be determined from P-V-T and phase equilibrium data represents an important contribution to the ever increasing knowledge of physical and chemical laws that are the fundamental basis of the vast chemical industry.

Now that use of high pressures and temperatures is commonplace in the petroleum industry, the demand for high-pressure thermodynamic data is exceedingly great. To keep abreast of modern trends that demand more P-V-T data of higher quality, a laboratory was established and partly equipped in 1952 for accurate high-pressure investigations of the P-V-T relationships of hydrocarbons and petrochemicals. In the past year, the P-V-T laboratory has been essentially completed. Most of the intricate, highly specialized equipment required for this work was not available commercially and was designed and fabricated to a large extent by Bureau of Mines personnel. A portion of the equipment designed for experimental studies up to 5,000-pounds-per-square inch pressure and up to 660° F. is illustrated by the composite photograph of figure 22. The newly designed air-or-inert-gas thermostat incorporates many advantages in addition to making it possible to work easily at temperatures 100° higher than the maximum working temperature obtainable in the liquid filled thermostat usually employed in this type of investigation.

Trial tests and calibration work are already underway with this new equipment, and the laboratory will soon be ready for use on a continuing, coordinated program of P-V-T studies. These studies will be made on pure materials and mixtures of pure materials that have been isolated from petroleum and natural gas. Also, many of the natural and synthesized compounds produced as intermediates or finished products in refining and chemical process operations will be studied. The types of materials for which investigations are planned comprise literally hundreds of different relatively important substances and, in addition to hydrocarbons, include classes of sulfur, nitrogen, and halogenated and oxygenated compounds.

Statistical Mechanical Calculations

The theoretical calculations of thermodynamic properties bring together and extend the results of the experimental studies. The culmination of a series of investigations of the properties of a partial compound is the preparation by methods of theoretical chemistry of extensive tables of all its important thermodynamic properties over a range of temperatures (-460° to +1,500° F. or higher) of greatest practical applicability. Such complete tables of thermodynamic data were prepared



A

B

C

Figure 22. - Pressure-volume-temperature apparatus showing the (A) compressibility bench, (B) thermostat, and (C) control panel.

for furan,[65] thiacyclobutane,[61] thiacyclopentane,[66] 3-thiapentane,[67] 3-methylthiophene,[59] thiacyclohexane (manuscript in preparation), 2-methyl-2-propanethiol,[68] and 2,2,3-tri-methylbutane.[69]

Because elemental sulfur may be present in crude petroleum or intermediate petroleum products, and as it is often encountered in reactions involving sulfur compounds, a knowledge of the thermodynamic properties of this element is important. Consequently, the existing thermodynamic data for elemental sulfur are being correlated and extended by theoretical methods. This work has helped to put the thermodynamic data for elemental sulfur into a more useful form and has pointed out deficiencies in the existing body of data. An oral report of this work was made at a recent national American Chemical Society meeting.

TRANSPORTATION OF NATURAL GAS

Flow of Natural Gas in High Reynolds Number Pipelines

This research was undertaken in 1946 in cooperation with the American Gas Association. The objectives were to review the literature and present use of pipeline formulas to develop the relationship between friction factor[70] and Reynolds number for supersmooth (gun-barrel finish) pipe and commercial pipes, and to determine factors useful in the design of long pipeline systems. The first and second parts of the study have been completed, and the third part will be completed by the end of 1953.

Concurrently with the review of literature on the flow of fluids, equipment was assembled and facilities were constructed for determining friction factors for the flow of gas in pipe at the Cliffside field near Amarillo, Tex. Friction factors were determined for the flow of gas through 2-inch seamless, extra heavy, grade B, commercial pipe for Reynolds numbers from 50,000 to 5 million. The work at the Cliffside field was discontinued in 1949, at which time additional test pipes were acquired and the equipment was redesigned and moved to a test site at Goleta, Calif., where conditions were considered to be more favorable for testing at high Reynolds

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[65] Guthrie, G. B., Jr. Scott, D. W., Hubbard, W. N., Katz, C., McCullough, J. P., Williamson, K. D., and Waddington, Guy, Thermodynamic Properties of Furan: Jour. Am. Chem. Soc., vol. 74, No. 18, Sept. 20, 1952, pp. 4662-4669.

[66] Hubbard, W. N., Finke, H. L., Scott, D. W., McCullough, J. P., Katz, C., Gross, M. E., Messerly, J. F., Pennington, R. E., and Waddington, Guy, Thiacyclopentane: Heat Capacity, Heats of Fusion and Vaporization, Vapor Pressure, Entropy, Heat of Formation and Thermodynamic Functions: Jour. Am. Chem. Soc., vol. 74, No. 23, Dec. 5, 1952, pp. 6025-6030.

[67] Scott, D. W., Finke, H. L., Hubbard, W. N., McCullough, J. P., Oliver, G. D., Gross, M. E., Katz, C., Williamson, K. D., Waddington, Guy, Huffman, H. M., 3-Thiapentane: Heat Capacity, Heats of Fusion and Vaporization, Vapor Pressure, Entropy, Heat of Formation and Thermodynamic Functions: Jour. Am. Chem. Soc., vol. 74, No. 18, Sept. 20, 1952, pp. 4656-4662.

[68] McCullough, J. P., Scott, D. W., Finke, H. L., Hubbard, W. N., Gross, M. E., Katz, C., Pennington, R. E., Messerly, J. F., and Waddington, Guy, The Thermodynamic Properties of 2-Methyl-2-propanethiol From 0° to 1,000° K.: Jour. Am. Chem. Soc., vol. 75, No. 8, Apr. 20, 1953, pp. 1818-1824.

[69] Scott, D. W., and Waddington, Guy, Thermodynamic Functions of 2,2,3-Tri-methylbutane: Jour. Am. Chem. Soc., vol. 75, No. 8, Apr. 20, 1953, pp. 2006-2007.

[70] As used in this report, the term "friction factor" indicates $\sqrt{1/f}$ where f is the friction coefficient commonly used in flow equations. However, several writers have used the terms "friction factor" and "friction coefficient" interchangeably. This practice is not being followed in this report.

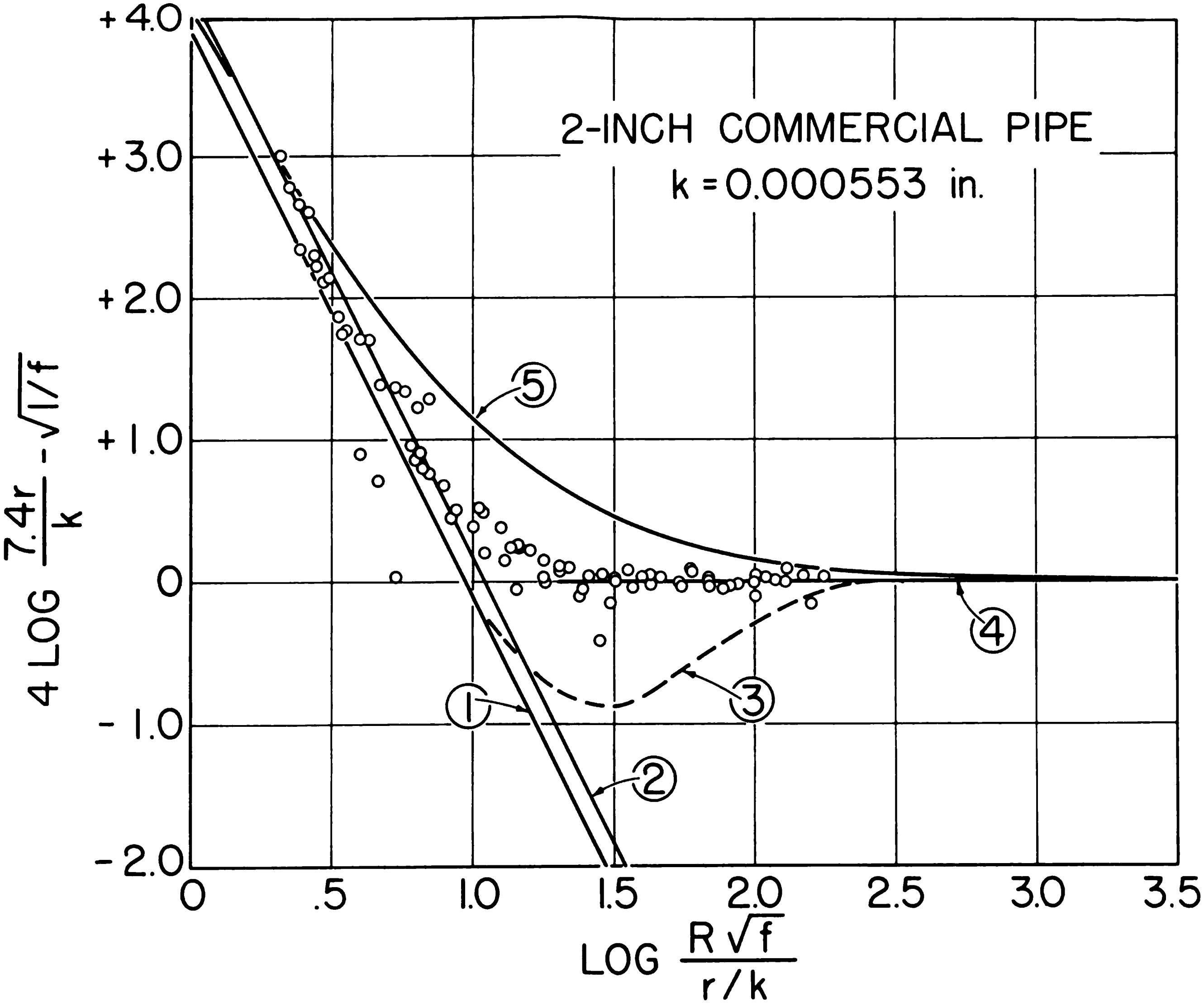

Figure 23. - Transition region characteristics for 2-inch commercial pipe.

numbers. At Goleta, friction factors were determined for 2-inch seamless, 3-inch welded, 3-inch seamless, 4-inch seamless, 6-inch seamless, 8-inch seamless, and 8-inch welded test sections of commercial pipe. In addition, a superfinished piece of stainless-steel pipe was tested, which had been honed on the inside to a "mirror" smooth surface with a very true circular shape with a diameter of 3.008 inches. The purpose of testing this pipe was to develop a standard for use as a comparison in studying the effect of surface roughness on friction factors.

In correlating the friction factors obtained from test data on the commercial pipe, it was found that, at the higher Reynolds numbers, the friction factor is independent of Reynolds number and is a function only of the relative roughness of the internal surface of the pipes. This relationship is clearly illustrated by the data in figure 23, which are typical of the data obtained for the commercial pipes. The coordinates of this figure were chosen to emphasize the trends in the data taken at the Cliffside field for the 2-inch commercial pipe. To the right of a value of 1.5 on the abscissa (log $\frac{R\sqrt{f}}{r/k}$), the data follow the resistance equation (curve 4) of Nikuradse[71] for flow in rough pipes. At values below 1.5 and above 0.9 on the abscissa the data show the transition between smooth- and rough-turbulent flow. Below 0.9 where the flow was smooth-turbulent the data form a straight line, which is indicated by curve 2. The resistance equation of Nikuradse[72] for flow in smooth pipes is represented by curve 1, which is parallel to curve 2. Curve 3 shows the transition relationship that Nikuradse[71] found for pipes coated internally with uniform sand grains. Curve 5 represents the Colebrook[73] equation, which is commonly used to show the relationship between friction factor and relative roughness and Reynolds number.

A comprehensive publication is planned for the near future giving results and correlations of the experimental work on the flow of natural gas through short experimental pipelines, the effect of liquids and dust on pipeline performance, and design factors for long pipelines.

Underground Storage of Natural Gas

Although the natural gas industry in the United States originated in the Appalachian region, that area now consumes more than twice as much natural gas as it produces. In the region there are 101 storage fields, with a combined capacity exceeding 526,000,000 cu. ft., which are vital to the continued use of natural gas by the large number of consumers. A report[74] describing the hazards involved in underground storage of natural gas in coal-mining areas emphasizes that storage fields must be developed with due consideration of the rights and safety of the coal industry, problems can be solved by complete cooperation between the two industries and their mutual enlightenment through free exchange of information, and the competitive relationship between the two industries must not become a stumbling block in the way of safety and public interest.

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[71] Nikuradse, J., Stromungsgestetze in Rauhen Rohren: V.D.I. Forschungsheft 361, 1933; trans., Laws of Fluid Flow in Rough Pipe: Petrol. Eng., vol. 11, 1940, pt. 1 March, pp. 164-166; pt 2 May, pp. 75-82; pt. 3 June, pp. 124-130; pt. 4 July, pp. 38-42; pt. 5 August, pp. 83-87.

[72] Nikuradse, J., Gesetzmassigkeiten der Turbulenten Stromung in Glatten Rohren. V.D.I. Forschungsheft No. 356, 1932.

[73] Colebrook, C. F., Turbulent Flow in Pipes, With Particular Reference to the Transition Region Between the Smooth and Rough Pipe Laws. Jour. Inst. Civil Eng. (London), vol. 11, 1938-1939, pp. 133-156.

[74] Wheeler, H. P., Jr., and Eckard, W. E., Underground Storage of Natural Gas in Coal-Mining Areas: Bureau of Mines Inf. Circ. 7654, 1952, 11 pp.; also Gas Age, vol. 111, No. 5, Feb. 26, 1953, pp. 28-31, 68-71; also Petrol. Eng., vol. 25, No. 4, April 1953, pp. D-42 and D-50.